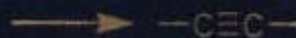


Comprehensive Organic Transformations

A Guide to Functional
Group Preparations

Second Edition

Richard C. Larock



COMPREHENSIVE ORGANIC TRANSFORMATIONS

**A Guide to
Functional Group Preparations
Second Edition**

**By
Richard C. Larock**



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**TO JOHN
FOR EVERYTHING**

FOREWORD

The first edition of this book, *Comprehensive Organic Transformations – A Guide to Functional Group Transformations*, which appeared in 1989, delivered in abundance the information promised by the title. It was truly comprehensive, as it covered countless reactions (starting from or leading to the core functional groups of organic chemistry, from $C=C$ to hydroxyl and amino to carbonyl to carboxylic acid and derivatives), and contained zillions of useful references. Packed within a thousand or so pages was an enormous amount of valuable and readily located synthetic chemistry, covering the literature up to 1987 (mainly from 1950–1987).

No wonder then that Richard Larock's *Comprehensive Organic Transformations* treatise became a mainstay of academic and industrial synthetic chemists, a great place to look when confronted with a new problem or task. For students, *Comprehensive Organic Transformations* has served as a concentrated one-volume guide to synthesis, and as a way to deepen and broaden their command of the vast body of knowledge that is synthetic chemistry. It is precisely because *Comprehensive Organic Transformations* has been of such value to chemists that its devotees, including myself, have hoped that an updated version would be forthcoming as an aid to keeping abreast of the avalanche of new developments in the field of synthesis. I've heard synthetic chemists joke that there are two types of colleagues: those who try to keep up with the literature and fail, and those who have stopped trying. Not so. Richard Larock is a different breed; he is still trying, and he has succeeded. In this new work, the second edition of *Comprehensive Organic Transformations*, Richard provides us with another scientific treasure chest and a powerful tool in dealing with the superhuman task of keeping up to date in chemistry.

In his Foreword to the first edition of *Comprehensive Organic Transformations*, H.C. Brown wrote "One must admire Richard Larock's courage in undertaking this monumental task". I agree completely. But, there is an additional comment that I am moved to make on the second edition: Thanks, Richard, for the valiant effort which produced this book; indeed, many thanks from us all.

E. J. Corey
Department of Chemistry & Chemical Biology
Harvard University

PREFACE

Organic synthesis is one of the most rapidly developing areas in all of chemistry. Every day useful new reagents and reactions are reported worldwide in the chemical literature. It is increasingly difficult for the organic chemist to keep up with the latest in synthetic organic methodology without spending an inordinate amount of time reading a wide variety of chemical journals, including many whose focus is not strictly synthetic organic chemistry.

In recent years, a variety of reviews, books and multi-volume treatises have appeared to aid the organic chemist interested in synthetic methodology, but many of these are either inconvenient, limited in scope, or prohibitively expensive for personal use or for those just entering the field. The intent of the present volume is to provide a comprehensive, highly condensed, systematic collection of useful synthetic methodology that both the beginning student and the long-time practitioner of organic synthesis will find useful.

This book began in 1973 as a series of graduate course handouts on the most important methodology for the synthesis of the major organic functional groups. Like the aforementioned publications, this reference work grew rapidly over the years to a major treatise covering a vast amount of synthetic organic chemistry. In the mid 1980's it was felt that the synthetic organic chemistry community might benefit from this compilation, so a serious effort was made to thoroughly update and organize the material for publication. The result was the first edition of *Comprehensive Organic Transformations*, which appeared in late 1989, and covered the literature through 1987. With the success of that first edition and the continuing need for a single, comprehensive inexpensive compilation on organic synthetic methodology, the author was encouraged to attempt the present major update.

The author takes full responsibility for the reactions, reagents and references covered. In choosing material for this text, the author has observed the following general guidelines. All reactions covered should be either very general in scope or else so unique that the methodology will find real synthetic utility. Yields should generally be at least 50%. Reagents should be readily available or easily prepared and handled in the laboratory. As much as possible, similar transformations appear together in as concise a format as possible. Significant limitations in methodology are noted. No effort has been made to cover the use of protecting groups, since excellent reviews on this subject are already available. Likewise, heterocyclic chemistry has consciously been omitted, except where heterocycles have been employed to effect simple functional group manipulations. Synthetically useful, multiple functional group transformations have been covered and cross-referenced in appropriate sections, although they present certain organizational problems. To those chemists whose contributions to synthetic methodology may have been slighted or altogether ignored, I apologize. It would be appreciated if major errors or omissions are brought to the author's attention, so that future printings and subsequent editions may be corrected.

As in the first edition, all reactions have been systematically organized according to the functional group being synthesized, with no attempt to cover the less important functional groups. Within each chapter, the methodology is further subdivided into major processes, such as oxidation, reduction, alkylation, etc. It is hoped that the reader will easily find the desired transformation by skimming the detailed Table of Contents, although an extensive Transformation Index is available.

The first edition of *Comprehensive Organic Transformations* covered some 160 or more primary chemical journals and a number of books and reviews published up to 1987. The present update has been generated by carefully scanning every page of the *Journal of the American Chemical Society*, the *Journal of Organic Chemistry*, *Tetrahedron Letters* and *Synlett* for the years 1988 through 1995, and checking references therein for additional material. Unfortunately, there simply was not enough time available to the author to review the other major, synthetic organic chemistry journals, as thoroughly. Thirty nine new journals and numerous additional reviews and books have been covered in this edition. Obscure journals not readily available to most synthetic organic chemists have been avoided. The names of authors have been omitted to save space. Original publications describing a new transformation have usually been cited, but they have on occasion been omitted if they do not necessarily describe the best reaction conditions for running the reaction or purvey little of the scope of the reaction. References containing full experimental procedures, though they may be buried in an experimental section, have been favored over communications lacking such details. An attempt has been made to highlight reviews and significant publications. The immediate problem one encounters is in deciding where to draw the line on references. Initial reports of a useful, new reaction have received complete coverage. However, a time soon comes when a truly significant reaction, such as the use of ester enolates in synthesis, appears routinely in publication after publication and no reviews have appeared. In such situations, the author has tended to include most of the new material and has not had the time to omit the more inconsequential earlier references.

It is hoped that the reader finds this latest effort worthwhile and will not hesitate to make suggestions on ways this material may be improved. Corrections, additions and suggestions would be deeply appreciated.

Richard C. Larock
Ames, Iowa USA

ABOUT THE AUTHOR

Richard C. Larock was born in Berkeley, California, in 1944 and raised in the San Francisco Bay Area.

He received his B.S. degree *summa cum laude* in chemistry, at the University of California at Davis, in 1967. While there, he participated in the University of California Education Abroad Program in Göttingen, West Germany, and did undergraduate research with Professor George Zweifel. He was also elected to Phi Kappa Phi and Phi Beta Kappa National Honor Societies and received the Outstanding Achievement Award in the Department of Chemistry, and the Herbert A. Young Award for highest achievement in the College of Letters and Science.

Dr. Larock received an NSF Graduate Fellowship to pursue his graduate training at Purdue University, working with 1979 Nobel Laureate, Herbert C. Brown, on the mercuration of organoboranes. After obtaining his Ph.D. in 1971, he received an NSF Postdoctoral Fellowship to work with 1990 Nobel Laureate, E. J. Corey, at Harvard University.

In 1972, he joined the organic chemistry faculty at Iowa State University, where he is presently University Professor of Chemistry. His early work at Iowa State, on new applications of organomercurials in organic synthesis, earned him an Alfred P. Sloan Foundation Fellowship and a DuPont Young Faculty Scholarship, and culminated in the publication of two books in the area: *Organomercury Compounds in Organic Synthesis* and *Solvomercuration/Demercuration Reactions in Organic Synthesis*.

Dr. Larock's use of organomercurials to generate synthetically valuable organopalladium intermediates encouraged him to move into the exciting new field of organopalladium chemistry, where his scientific contributions have involved the application of vinylpalladium chemistry to organic synthesis, the discovery of new routes to π -allylpalladium compounds, the development of new methodology based on palladium migration chemistry, the synthesis of prostaglandins *via* palladium intermediates, and most recently, palladium(II)-catalyzed cyclizations and oxidations, and the palladium(0)-catalyzed annulation of alkenes, dienes and alkynes. This work has been described in over 150 publications and 30 patents. Current interests also include the synthesis of industrially useful oils and biodegradable polymers from natural oils, particularly soybean oil.

Dr. Larock has recently been awarded 1997 and 1998 Merck Academic Development Awards in Chemistry, received a 1998 Regent's Award for Faculty Excellence at Iowa State University, and in 1999 been named University Professor of Chemistry.

ACKNOWLEDGMENTS

The preparation of a book of this magnitude requires the assistance of a number of people. The author is indebted to Iowa State University for providing the time and assistance necessary for the preparation of much of this book, and a faculty improvement leave in 1994 to help get this second edition off the ground. The Department of Chemistry at the University of Hawaii at Manoa is gratefully acknowledged for having provided a visiting professorship in 1985 (which allowed the author to push the original manuscript through to publication), and an office during my 1994 faculty improvement leave.

To all those around me who have had to "endure" this book for so long, your encouragement, patience and perseverance are deeply appreciated. The author is particularly indebted to Professor John Maves for all the personal impositions created by this entire endeavor. I thank my students – who have often had to take a back seat to this project – for their understanding and patience.

I must also acknowledge a core of dedicated secretaries, who over the years continually updated the early material for classroom use, particularly Mrs. Helen Eggleston and Mrs. Denise Junod. The author is especially indebted to Mrs. Nancy Qvale, who was responsible for the preparation of a major portion of the final manuscript for the first edition.

Finally, the author wishes to thank his parents Hazel and Ralph Larock for having provided genes with the perseverance and perfectionism necessary to complete this project, when it seemed that the project would never end.

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10. MISCELLANEOUS REACTIONS 1995**TRANSFORMATION INDEX 1997**

LITERATURE ABBREVIATIONS

Acct Chem Res	<i>Accounts of Chemical Research</i>
Acta Chem Scand	<i>Acta Chemica Scandinavica</i>
Acta Chem Scand B	<i>Acta Chemica Scandinavica. Series B: Organic Chemistry and Biochemistry</i>
Acta Chimica Sinica	<i>Acta Chimica Sinica</i>
Adv Alicyclic Chem	<i>Advances in Alicyclic Chemistry</i>
Adv Biochem Eng	<i>Advances in Biochemical Engineering</i>
Adv Carbohydr Chem	<i>Advances in Carbohydrate Chemistry</i>
Adv Catalysis	<i>Advances in Catalysis</i>
Adv Chem Ser	<i>Advances in Chemistry Series</i>
Adv Heterocyclic Chem	<i>Advances in Heterocyclic Chemistry</i>
Adv Org Chem	<i>Advances in Organic Chemistry: Methods and Results</i>
Adv Organometal Chem	<i>Advances in Organometallic Chemistry</i>
Adv Photochem	<i>Advances in Photochemistry</i>
Adv Phys Org Chem	<i>Advances in Physical Organic Chemistry</i>
Agric Biol Chem	<i>Agricultural and Biological Chemistry</i>
Anal Chem	<i>Analytical Chemistry</i>
Anal de Quim	<i>Anales de Quimica</i>
Angew	<i>Angewandte Chemie</i>
Angew Int	<i>Angewandte Chemie, International Edition in English</i>
Ann	<i>Justus Liebig's Annalen der Chemie</i>
Ann Chim	<i>Annales de Chimie</i>
Ann Chim (Rome)	<i>Annali di Chimica (Rome)</i>
Ann NY Acad Sci	<i>Annals of the New York Academy of Sciences</i>
Ann Rep Med Chem	<i>Annual Reports in Medicinal Chemistry</i>
Appl Environ Microbiol	<i>Applied and Environmental Microbiology</i>
Appl Microbiol	<i>Applied Microbiology</i>
Appl Microbiol Biotechnol	<i>Applied Microbiology and Biotechnology</i>
Appl Radiat Isot	<i>Applied Radiation and Isotopes</i>
Arch Biochem Biophys	<i>Archives of Biochemistry and Biophysics</i>
Arch Pharm	<i>Archiv der Pharmazie</i>
Arkiv Kemi	<i>Arkiv for Kemi</i>
Arzneim Forsch	<i>Arzneimittel-Forschung</i>
Austral J Chem	<i>Australian Journal of Chemistry</i>
BCSJ	<i>Bulletin of the Chemical Society of Japan</i>
Ber	<i>Berichte der Deutschen Chemischen Gesellschaft</i>
Biocatalysis	<i>Biocatalysis</i>
Biochem	<i>Biochemistry</i>
Biochem Biophys Res Commun	<i>Biochemical and Biophysical Research Communications</i>
Biochem J	<i>Biochemical Journal</i>
Biochim Biophys Acta	<i>Biochimica et Biophysica Acta</i>
Bio Med Chem Lett	<i>Bioorganic and Medicinal Chemistry Letters</i>


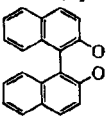
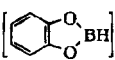
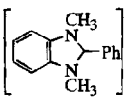
Bioorg Chem	<i>Bioorganic Chemistry</i>
BSCF	<i>Bulletin de la Societe Chimique de France</i>
Bull Acad Polon Sci, Ser Sci Chem	<i>Bulletin de l'Academie Polonaise des Sciences, Serie des Sciences Chimiques</i>
Bull Acad Sci USSR, Div Chem Sci	<i>Bulletin of the Academy of Sciences of the USSR, Division of Chemical Science</i>
Bull Korean Chem Soc	<i>Bulletin of the Korean Chemical Society</i>
Bull Russ Acad Sci, Div Chem Sci	<i>Bulletin of the Russian Academy of Sciences, Division of Chemical Sciences</i>
Bull Soc Chim Belg	<i>Bulletin des Societes Chimiques Belges</i>
CA	<i>Chemical Abstracts</i>
Can J Chem	<i>Canadian Journal of Chemistry</i>
Cancer Lett	<i>Cancer Letters</i>
Carbohydr Res	<i>Carbohydrate Research</i>
Catal Rev	<i>Catalysis Reviews</i>
CC	<i>Journal of the Chemical Society: Chemical Communications</i>
Chem Eng News	<i>Chemical and Engineering News</i>
Chem in Britain	<i>Chemistry in Britain</i>
Chem Ind	<i>Chemistry and Industry</i>
Chem Listy	<i>Chemické Listy</i>
Chem Pharm Bull	<i>Chemical and Pharmaceutical Bulletin</i>
Chem Phys Lipids	<i>Chemistry and Physics of Lipids</i>
Chem Rev	<i>Chemical Reviews</i>
Chem Scripta	<i>Chemica Scripta</i>
Chem Soc Rev	<i>Chemical Society Reviews</i>
Chem Weekb	<i>Chemisch Weekblad</i>
Chem Zeitung	<i>Chemiker Zeitung</i>
Chem Zentr	<i>Chemisches Zentralblatt</i>
Chimia	<i>Chimia</i>
Chim Ind (Milan)	<i>Chimica e l'Industria (Milan)</i>
CL	<i>Chemistry Letters</i>
Coll Czech Chem Commun	<i>Collection of Czechoslovak Chemical Communications</i>
Compt Rend	<i>Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences</i>
Compt Rend C	<i>Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences. Serie C: Sciences Chimiques</i>
Curr Sci	<i>Current Science</i>
Discuss Faraday Soc	<i>Discussions of the Faraday Society</i>
Dokl	<i>Proceedings of the Academy of Sciences of the USSR, Chemistry Section</i>
Experientia	<i>Experientia</i>
Fortschr Chem Forsch	<i>Fortschritte der Chemischen Forschung</i>
Fund Res Homogeneous Catal	<i>Fundamental Research in Homogeneous Catalysis</i>
Gazz Chim Ital	<i>Gazzetta Chimica Italiana</i>
Helv	<i>Helvetica Chimica Acta</i>
Heterocycles	<i>Heterocycles</i>

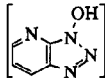
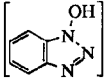

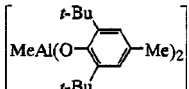
Ind Eng Chem	<i>Industrial and Engineering Chemistry</i>
Ind J Chem	<i>Indian Journal of Chemistry</i>
Ind J Chem B	<i>Indian Journal of Chemistry. Section B: Organic Chemistry and Medicinal Chemistry</i>
Inorg	<i>Inorganic Chemistry</i>
Int J Peptide Protein Res	<i>International Journal of Peptide and Protein Research</i>
Int J Sulfur Chem	<i>International Journal of Sulfur Chemistry</i>
Intra-Science Chem Reports	<i>Intra-Science Chemistry Reports</i>
Israel J Chem	<i>Israel Journal of Chemistry</i>
Izv Akad Nauk SSSR, Ser Khim	<i>Izvestiia Akademii Nauk SSSR. Seriya Khimicheskaya</i>
J Am Oil Chem Soc	<i>Journal of the American Oil Chemists' Society</i>
J Am Pharm Assoc	<i>Journal of the American Pharmaceutical Association</i>
J Antibiotics	<i>Journal of Antibiotics</i>
J Bacteriol	<i>Journal of Bacteriology</i>
J Biochem (Tokyo)	<i>Journal of Biochemistry (Tokyo)</i>
J Biol Chem	<i>Journal of Biological Chemistry</i>
J Catalysis	<i>Journal of Catalysis</i>
J Chem Ed	<i>Journal of Chemical Education</i>
J Chem Eng Data	<i>Journal of Chemical and Engineering Data</i>
J Chem Res (S)	<i>Journal of Chemical Research. Synopses</i>
J Fluorine Chem	<i>Journal of Fluorine Chemistry</i>
J Gen Chem USSR	<i>Journal of General Chemistry of the USSR</i>
J Gen Microbiol	<i>Journal of General Microbiology</i>
J Heterocyclic Chem	<i>Journal of Heterocyclic Chemistry</i>
J Ind Chem Soc	<i>Journal of the Indian Chemical Society</i>
J Korean Chem Soc	<i>Journal of the Korean Chemical Society</i>
J Label Compds	<i>Journal of Labelled Compounds</i>
J Label Cpds Radiopharm	<i>Journal of Labelled Compounds and Radiopharmaceuticals</i>
J Lipid Res	<i>Journal of Lipid Research</i>
J Med Chem	<i>Journal of Medicinal Chemistry</i>
J Mol Catal	<i>Journal of Molecular Catalysis</i>
J Nat Prod	<i>Journal of Natural Products</i>
J Nucl Med	<i>Journal of Nuclear Medicine</i>
J Pharm Sci	<i>Journal of Pharmaceutical Sciences</i>
J Photochem	<i>Journal of Photochemistry</i>
J Phys Chem	<i>Journal of Physical Chemistry</i>
J Phys Org Chem	<i>Journal of Physical Organic Chemistry</i>
J Polym Sci, Polym Chem Ed	<i>Journal of Polymer Science: Polymer Chemistry Edition</i>
J Prakt Chem	<i>Journal für Praktische Chemie</i>
J Russ Phys Chem Soc	<i>Journal of the Russian Physical Chemical Society</i>
J Sci Ind Res B	<i>Journal of Scientific and Industrial Research. Part B: Physical Sciences</i>
J Vitaminol (Osaka)	<i>Journal of Vitaminology</i>
JACS	<i>Journal of the American Chemical Society</i>
JCS	<i>Journal of the Chemical Society</i>
JCS A	<i>Journal of the Chemical Society. Section A: Inorganic, Physical and Theoretical</i>
JCS B	<i>Journal of the Chemical Society. Section B: Physical Organic</i>
JCS C	<i>Journal of the Chemical Society. Section C: Organic</i>

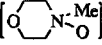



JCS D	<i>Journal of the Chemical Society, Section D: Chemical Communications</i>
JCS Dalton	<i>Journal of the Chemical Society: Dalton Transactions</i>
JCS Japan	<i>Journal of the Chemical Society of Japan</i>
JCS Perkin I	<i>Journal of the Chemical Society: Perkin Transactions I</i>
JCS Perkin II	<i>Journal of the Chemical Society: Perkin Transactions II</i>
JOC	<i>Journal of Organic Chemistry</i>
JOC USSR	<i>Journal of Organic Chemistry of the USSR</i>
JOMC	<i>Journal of Organometallic Chemistry</i>
Macromolecules	<i>Macromolecules</i>
Mendeleev Commun	<i>Mendeleev Communications</i>
Methods Carbohydr Chem	<i>Methods in Carbohydrate Chemistry</i>
Monatsh	<i>Monatshefte für Chemie</i>
Natl Prod Repts	<i>Natural Product Reports</i>
Nature	<i>Nature</i>
Naturwiss	<i>Naturwissenschaften</i>
Newer Methods Prep Org Chem	<i>Newer Methods of Preparative Organic Chemistry</i>
Nouv J Chim	<i>Nouveau Journal de Chimie</i>
Nucleosides and Nucleotides	<i>Nucleosides and Nucleotides</i>
Org Mag Res	<i>Organic Magnetic Resonance</i>
Org Photochem	<i>Organic Photochemistry</i>
Org Prep Proc	<i>Organic Preparations and Procedures</i>
Org Prep Proc Int	<i>Organic Preparations and Procedures International</i>
Org Rxns	<i>Organic Reactions</i>
Org Syn	<i>Organic Syntheses</i>
Org Syn Coll Vol	<i>Organic Syntheses. Collective Volume</i>
Organomet	<i>Organometallics</i>
Organomet Chem Rev A	<i>Organometallic Chemistry Reviews. Section A: Subject Reviews</i>
Organomet Chem Syn	<i>Organometallics in Chemical Synthesis</i>
Phosphorus	<i>Phosphorus and the Heavier Group Va Elements</i>
Phosphorus and Sulfur	<i>Phosphorus and Sulfur and the Related Elements</i>
Photochem Photobiol	<i>Photochemistry and Photobiology</i>
Phytochemistry	<i>Phytochemistry</i>
Pol J Chem	<i>Polish Journal of Chemistry</i>
Polym J	<i>Polymer Journal</i>
Proc Acad Sci USSR, Chem Sec	<i>Proceedings of the Academy of Sciences of the USSR. Chemistry Section</i>
Proc Chem Soc	<i>Proceedings of the Chemical Society (London)</i>
Proc Ind Acad Sci A	<i>Proceedings—Indian Academy of Sciences. Section A, Part 1: Chemical Sciences</i>
Proc Natl Acad Sci USA	<i>Proceedings of the National Academy of Sciences of the United States of America</i>
Prog Inorg Chem	<i>Progress in Inorganic Chemistry</i>
Prostaglandins	<i>Prostaglandins</i>
PSS	<i>Phosphorus, Sulfur, and Silicon and the Related Elements</i>

Pure Appl Chem	<i>Pure and Applied Chemistry</i>
Quart Rev	<i>Quarterly Reviews—Chemical Society, London</i>
Rec Chem Prog	<i>Record of Chemical Progress</i>
Rec Trav Chim	<i>Recueil des Travaux Chimiques des Pays-Bas</i>
Recl J R Neth Chem Soc	<i>Recueil: Journal of the Royal Netherlands Chemical Society</i>
Rev Chem Intermed	<i>Reviews of Chemical Intermediates</i>
Rev Pure Appl Chem	<i>Reviews of Pure and Applied Chemistry</i>
Rocz	<i>Roczniki Chemii</i>
Russ Chem Rev	<i>Russian Chemical Reviews</i>
Russ J Chem	<i>Russian Journal of Chemistry</i>
S Afr J Chem	<i>South African Journal of Chemistry</i>
SL	<i>Synlett</i>
Soc Chem Ind	<i>Society of Chemical Industry, London Chemical Engineering Group, Proceedings</i>
Steroids	<i>Steroids</i>
Syn	<i>Synthesis</i>
Syn Commun	<i>Synthetic Communications</i>
Tetr	<i>Tetrahedron</i>
Tetr Asym	<i>Tetrahedron: Asymmetry</i>
TL	<i>Tetrahedron Letters</i>
Topics Curr Chem	<i>Topics in Current Chemistry</i>
Topics Stereochem	<i>Topics in Stereochemistry</i>
Trans Faraday Soc	<i>Transactions of the Faraday Society</i>
Transition Met Chem	<i>Transition Metal Chemistry (New York)</i>
Z. Chem	<i>Zeitschrift für Chemie</i>
Z. Naturforsch B	<i>Zeitschrift für Naturforschung. Teil B: Anorganische Chemie, Organische Chemie, Biochemie, Biophysik, Biologie</i>
Zh Obshch Khim	<i>Zhurnal Obshchei Khimii</i>

CHEMICAL ABBREVIATIONS

Ac	acetyl
acac	acetylacetonate [$\text{CH}_3\text{COCHCOCH}_3$]
acaen	<i>N,N'</i> -bis(1-methyl-3-oxobutylidene)ethylenediamine
AIBN	2,2'-azobisisobutyronitrile [$\text{Me}_2\text{C}(\text{CN})\text{N}=\text{N}(\text{CN})\text{Me}_2$]
Am	amyl
aq	aqueous
Ar	aryl
	9-borabicyclo[3.3.1]nonyl
9-BBN	9-borabicyclo[3.3.1]nonane
BINAP	2,2'-bis(diphenylphosphino)-1,1'-binaphthyl
BINOL	
bipy	2,2'-bipyridyl
Boc	<i>tert</i> -butoxycarbonyl
Bu	butyl
<i>c</i>	cyclo
CAN	ceric ammonium nitrate
cat	catalytic
CB	catecholborane 
COD	<i>cis,cis</i> -1,5-cyclooctadiene
COT	1,3,5-cyclooctatriene
Cp	cyclopentadienyl
Cy	cyclohexyl
DABCO	1,4-diazabicyclo[2.2.2]octane
DBA	dibenzylideneacetone [$\text{PhCH}=\text{CHCOCH}=\text{CHPh}$]
DBN	1,5-diazabicyclo[4.3.0]non-5-ene
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	dicyclohexylcarbodiimide
DDQ	2,3-dichloro-5,6-dicyano-1,4-benzoquinone
DEAD	diethyl azodicarboxylate
dip	(2,3)-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane
DMAP	4-dimethylaminopyridine
DMBI	1,3-dimethyl-2-phenylbenzimidizoline 

DME	1,2-dimethoxyethane
DMF	<i>N,N</i> -dimethylformamide
DMSO	dimethylsulfoxide
dppb	1,4-bis(diphenylphosphino)butane $[\text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2]$
dppe	1,2-bis(diphenylphosphino)ethane $[\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2]$
dppf	1,1'-bis(diphenylphosphino)ferrocene
dppp	1,3-bis(diphenylphosphino)propane $[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{PPh}_2]$
E ⁺	electrophile
EDA	ethylenediamine $[\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2]$
EDTA	ethylenediaminetetraacetate
Et	ethyl
Fer	ferrocenyl
fod	6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato $[\text{CF}_3\text{CF}_2\text{CF}_2\text{COCHCOC}(\text{CH}_3)_3]$
Fp	dicarbonyl(η^5 -cyclopentadienyl)iron(I) $[\text{Fe}(\text{CO})_2(\text{cyclopentadienyl})]$
Het	heterocycle
hfacac	1,1,1,5,5,5-hexafluoroacetylacetonate $[\text{CF}_3\text{COCHCOCF}_3]$
HMPA = HMPT	hexamethylphosphoramide
HOAt	1-hydroxy-7-azabenzotriazole 
HOBT	1-hydroxybenzotriazole 
<i>i</i>	iso
lpc	isopinocampheyl 
L	ligand
LDA	lithium diisopropylamide $[\text{LiN}(i\text{-C}_3\text{H}_7)_2]$
<i>m</i>	meta
MAD	methylaluminum bis(2,6-di- <i>t</i> -butyl-4-methylphenoxide)
	
Me	methyl
MEM	methoxyethoxymethyl $[\text{CH}_3\text{OCH}_2\text{CH}_2\text{OCH}_2\text{-}]$
Mes	mesityl
mesal	<i>N</i> -methylsalicylaldimine
MOM	methoxymethyl $[\text{CH}_3\text{OCH}_2\text{-}]$
Ms	methanesulfonyl
<i>n</i>	normal

NADPH	nicotinamide adenine dinucleotide phosphate
NBA	<i>N</i> -bromoacetamide
NBD	norbornadiene
NBS	<i>N</i> -bromosuccinimide
NCS	<i>N</i> -chlorosuccinimide
NIS	<i>N</i> -iodosuccinimide
NMO	<i>N</i> -methylmorpholine oxide 
NMP	<i>N</i> -methyl-2-pyrrolidone
Nuc	nucleophile
<i>o</i>	ortho
<i>p</i>	para
PCC	pyridinium chlorochromate
PDC	pyridinium dichromate
PEG-400	poly(ethylene glycol)-400
Ph	phenyl
phen	1,10-phenanthroline
PPA	polyphosphoric acid
PPTS	pyridinium <i>p</i> -toluenesulfonate
Pr	propyl
py	pyridine
R	an organic group
R _f	perfluoroalkyl
Salen	<i>N,N'</i> -ethylenbis(salicylideneiminato)
salophen	<i>o</i> -phenylenebis(salicylideneiminato)
sec	secondary
Sia	1,2-dimethylpropyl [(CH ₃) ₂ CHCH ₂ CH ₃]
S,S-chiraphos	(<i>S,S</i>)-2,3-bis(diphenylphosphino)butane [(<i>S,S</i>)-Ph ₂ PCH(CH ₃)CH(CH ₃)PPh ₂]
<i>t</i>	tertiary
TCNE	tetracyanoethylene
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl 
Tf	trifluoromethanesulfonyl
Th	2-thienyl 
THF	tetrahydrofuran
THP	2-tetrahydropyranyl
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine [Me ₂ NCH ₂ CH ₂ NMe ₂]
TMP	2,2,6,6-tetramethylpiperidine 
Tol	tolyl
tolbinap	2,2'-bis(di- <i>p</i> -tolylphosphino)-1,1'-binaphthyl
tp	tetraphenylporphyrin
Ts	<i>p</i> -toluenesulfonyl

ALKANES AND ARENES

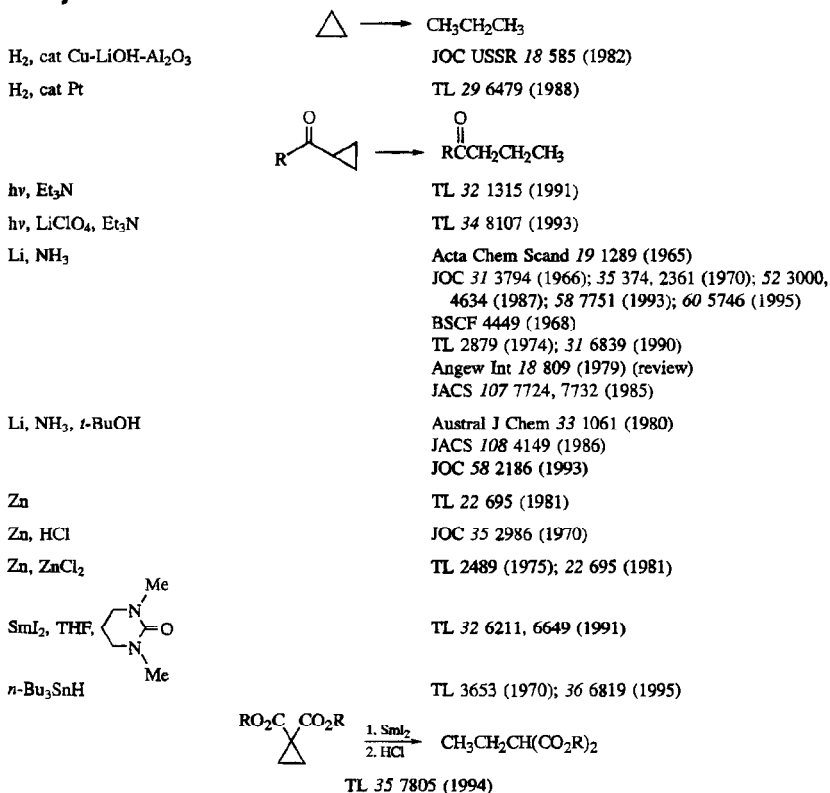
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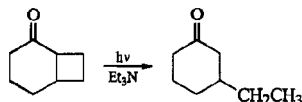
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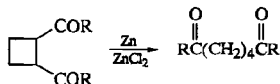
1. REDUCTION

1. Cyclic Alkanes





TL 32 1315 (1991)



TL 2489 (1975)

2. Arenes



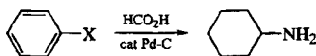
Reviews:

Adv Catalysis 16 124 (1966); 18 1 (1968)

P. N. Rylander, "Catalytic Hydrogenation in Organic Synthesis," Academic Press, New York (1979)

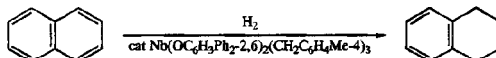
Acct Chem Res 12 324 (1979)

H ₂ , cat RuCl ₃ , cat (<i>n</i> -C ₈ H ₁₇) ₃ N	TL 36 885 (1995)
H ₂ , cat Ru-Al ₂ O ₃	JOC 37 2468 (1972); 53 3912 (1988); 56 1758, 4388 (1991)
H ₂ , cat π -C ₃ H ₅ CoL ₃	Inorg 15 2379 (1976)
H ₂ , cat Rh-Al ₂ O ₃	Adv Catalysis 9 727, 733 (1957) JOC 27 2288 (1962)
H ₂ , cat RhCl ₃ , cat (<i>n</i> -C ₈ H ₁₇) ₃ N	J Mol Catal 87 107 (1994)
H ₂ , cat RhCl ₃ , cat [(<i>n</i> -C ₈ H ₁₇) ₃ NCH ₃]Cl	TL 24 4139 (1983) J Mol Catal 34 221 (1986) (naphthalenes); 39 185 (1987) (polycyclic arenes); 87 107 (1994) JOC 52 2804 (1987)
H ₂ , cat [RhCl(1,5-hexadiene)] ₂ , cat R ₄ NX	Organomet 2 1055 (1983)
H ₂ , cat [ClRh(C ₇ H ₅)] ₂ -polymer	CL 603 (1982)
H ₂ , cat Rh(I)-polymer	JOC 44 239 (1979) JACS 103 5096 (1981)
H ₂ , cat [Rh(C ₅ Me ₅)Cl ₂] ₂	CC 427 (1977) Acct Chem Res 11 301 (1978)
H ₂ , cat [Si]-ORh(allyl)H	JACS 103 5253 (1981)
H ₂ , Raney Ni	JOC 58 2110 (1993)
H ₂ , cat PtO ₂	JACS 50 1970 (1928); 67 272, 276, 279 (1945) JOC 53 873 (1988); 59 4297 (1994)



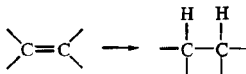
X = NO, N₃, NO₂, NH₂, NR₂

TL 33 7477 (1992)



JACS 114 1927 (1992)

3. Alkenes



3.1. Catalytic Hydrogenation

Reviews:

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3.1.1. Selective hydrogenation catalysts

5% Ru on Norit

IOC 24 708 (1959)

RuCl₂(PPh₃)₃

CL 1083 (1977) (polyenes to monoenes)

NaBH₄, CoCl₂ (mono > di > tri > tetrasubstituted)

IOC 44 1014 (1979)

JACS 108 67 (1986)

Rh-C

TL 32 2735 (1991) (fluoroalkenes); 36 7949 (1995) (enamide)

Rh-Al₂O₃

Org Syn Coll Vol 6 371 (1988)

TL 29 3171 (1988)

$\text{ClRh}(\text{PPh}_3)_3$ (Wilkinson's catalyst)	Discuss Faraday Soc 46 60 (1968) Chem Rev 21 73 (1973) Syn 329 (1978) Prog Inorg Chem 28 63 (1981)
$\text{ClRh}[\text{P}(p\text{-Tol})_3]_3$ (regioselective)	TL 33 5547 (1992)
$[\text{Rh}(\text{NBD})(\text{dppb})]\text{BF}_4$	CC 348 (1982) (syn to allylic, homoallylic OH) IACS 106 3866 (1984) (syn to OH); 107 4339 (1985) (syn to OH); 108 2476 (1986); 112 5290 (1990) (homoallylic OH) TL 25 4637 (1984) (allylic OH); 26 6005 (1985) (homoallylic OH); 28 3659 (1987)
$[\text{Rh}(\text{COD})(\text{dppb})]\text{BF}_4$	IACS 115 7152 (1993) TL 34 4939 (1993)
$[\text{Rh}(\text{NBD})(\text{dppb})]\text{OTf}$	Org Syn Coll Vol 8 420 (1993)
$[\text{Ir}(\text{COD})(\text{dppb})]\text{BF}_4$	TL 25 4637 (1984) (allylic OH)
$[\text{Ir}(\text{COD})(\text{py})(\text{PCy}_3)]\text{PF}_6$	TL 22 303 (1981) (α face of steroids); 25 4637 (1984) (allylic, homoallylic OH); 26 6005 (1985) (homoallylic OH) IACS 105 1072 (1983) (syn to OH); 106 3866 (1984) (syn to OH); 109 6493 (1987) (syn to CONR ₂); 113 4926, 4931 (1991) (syn to CONR ₂) Organomet 2 681 (1983) (syn to OH) JOC 50 5905 (1985) (syn to CO ₂ R, CONR ₂); 51 2655 (1986) (syn to OH, CO ₂ R, C=O, OMe); 60 5102 (1995) (syn to OH)
Nickel boride (P-2)	JOC 38 2226 (1973); 46 1263 (1981)
LaNi_5H_6	JOC 52 5695 (1987) (least substituted double bond)
NaH , $\text{NaO}-t\text{-Am}$, $\text{Ni}(\text{OAc})_2$	JOC 45 1937, 1946 (1980)
$\text{Pd}-\text{C}$	TL 32 2735 (1991) (fluoroalkenes)
$\text{Pd}-\text{BaSO}_4$	TL 32 2735 (1991) (fluoroalkenes)
Montmorillonite- PPh_2 - PdCl_2	TL 33 121 (1992)
$\text{Pd}(\text{hfacac})_2$, $\text{Me}_3\text{Si}(\text{OSiHMe})_n\text{OSiMe}_3$	TL 34 3075 (1993)
PtCl_2 , $(\text{Et}_4\text{N})\text{SnCl}_3$ or $(\text{Ph}_3\text{PMe})\text{SnBr}_3$	IACS 94 8716 (1972) (polyene to monoene)
PtO_2	Adv Catalysis 9 727 (1957)

3.1.2. Enantioselective hydrogenation catalysts


Reviews:

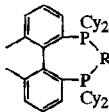
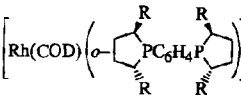
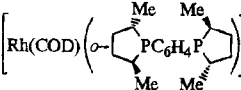
- H. B. Kagan, "Comprehensive Organometallic Chemistry," Eds. G. Wilkinson and F. G. A. Stone, Pergamon, Oxford (1982), Vol 8, p 463
Pure Appl Chem 56 99 (1984)
"Asymmetric Catalysis," Ed. B. Bosnich, NATO ASI Ser. E, No. 103, Martinus Nijhoff, Dordrecht (1986), Chpt 2
Chem Rev 92 1051 (1992) (asymmetric)

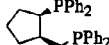
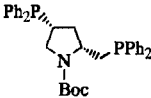
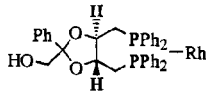
SL 169 (1992) (Rh bis-phosphines)

"Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 1

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21d, G. Thieme, Stuttgart-New York (1995), p 4239

Catalyst	Substrate	
 Ti(BINOL), <i>n</i> -BuLi, PhSiH ₃	trisubstituted aryl alkenes	IACS 115 12569 (1993)
Ru(DIPAMP)(2-Me-allyl) ₂ or Ru ₂ X ₂ (DIPAMP)	α,β -unsaturated carboxylic acids, α -amido acrylic acid	TL 33 5343 (1992)
Ru(2-Me-allyl)(diphosphine)	α,β -unsaturated carboxylic acid	Tetr Asym 2 43 (1991)
Ru ₂ Cl ₄ (BINAP)	α -amido- α,β -unsaturated lactam	TL 35 3239 (1994)
	enones	JOC 60 357 (1995)
Ru ₂ Cl ₄ (BINAP) ₂ (NEt ₃)	α -amidoacrylic acids	CC 922 (1985)
	unsaturated dicarboxylic acids	TL 28 1905 (1987); 35 835 (1994)
	α,β -unsaturated lactone and anhydride	TL 33 635 (1992)
	α -alkylidene lactams	TL 36 7379 (1995)
	2-fluoro-2-alkenoic acids	TL 33 7877 (1992)
	enones	JOC 60 357 (1995)
	vinyl ester	JOC 60 357 (1995)
	vinyl ether	JOC 60 357 (1995)
[(arene)RuX(BINAP)]X	allylic alcohol, α,β -unsat- urated carboxylic acid	CC 1208 (1989) JOC 59 3064 (1994)
	α,β -unsaturated lactone, enone	TL 33 635 (1992) JOC 60 357 (1995)
Ru(BINAP)(Ph)Cl	enamide	JOC 60 4324 (1995)
RuHCl(BINAP) ₂	α -amidoacrylic acids	CC 922 (1985)
	unsaturated dicarboxylic acids	TL 28 1905 (1987)
Ru(OAc) ₂ (BINAP)	enamides	JACS 108 7117 (1986) JOC 59 297 (1994)
	allylic alcohols	JACS 109 1596 (1987) JOC 53 708 (1988) TL 34 7359 (1993)
	homoallylic alcohols	JACS 109 1596 (1987)
	enone	TL 33 635 (1992) JOC 60 357 (1995)
	α -amido acrylate esters	JOC 59 3676 (1994)
	vinyl ether	JOC 60 357 (1995)
	vinyl ester	JOC 60 357 (1995)
	α,β -unsaturated carboxylic acid	JOC 52 3174 (1987) TL 31 7189 (1990) SL 501 (1994)

Catalyst	Substrate	
$\text{Ru}(\text{OAc})_2(\text{BINAP})$ (<i>continued</i>)	β,γ -unsaturated carboxylic acids	JOC 52 3174 (1987) TL 31 7189 (1990)
$\text{Ru}(\text{OAc})_2(\text{tolbinap})$	allylic alcohols	TL 31 549 (1990)
$\text{Ru}(\text{OAc})_2(\text{H}_8\text{-BINAP})$	α,β -unsaturated carboxylic acid	SL 501 (1994)
$\text{Ru}(\text{O}_2\text{CCF}_3)_2(\text{BINAP})$	allylic alcohols	TL 29 5343 (1988)
$[\text{Rh}(\text{NBD})\text{Cl}]_2, \text{Ph}_2\text{PCH}_2\text{CH}(\text{CH}_3)\text{PPh}_2$	α -amidoacrylic acids and esters	JOC 56 1783 (1991)
$[\text{Rh}(\text{NBD})_2]\text{ClO}_4, \text{Ph}_2\text{PCH}_2\text{CH}(\text{CH}_3)\text{PPh}_2$	α -amidoacrylic acids and esters	JACS 110 5491 (1978)
$[\text{Rh}(\text{COD})\text{Cl}]_2, \text{norphos}$	α -amidoacrylic acid	Angew Int 18 620 (1979)
$[\text{Rh}(\text{NBD})\text{Cl}]_2, \text{norphos}$	α -amidoacrylic acid and ester	JOC 56 1783 (1991)
$[\text{Rh}(\text{NBD})\text{Cl}]_2, S,S$ -chiraphos	α -amidoacrylic acid	JOC 56 1783 (1991)
$[\text{Rh}(\text{NBD})(S,S\text{-chiraphos})]\text{ClO}_4$	α -amidoacrylic acids and esters	JACS 99 6262 (1977); 115 4040 (1993) JOC 52 5143 (1987)
$[\text{Rh}(\text{NBD})(\text{BINAP})]\text{ClO}_4$	α -amidoacrylic acids α -amidoacrylic acids and esters	JACS 102 7932 (1980) Tetr 40 1245 (1984)
$[\text{Rh}(\text{NBD})(\text{BINAP})]\text{BF}_4$	α,β -unsaturated ester	JACS 108 2476 (1986)
 $\text{Rh}(\text{NBD})\text{X} \text{ (X = Cl, ClO}_4\text{)}$	α -amidoacrylate ester, itaconic acid and ester	TL 32 4745 (1991)
$[\text{Rh}(\text{NBD})(\text{Josiphos})]\text{BF}_4$	α,β -unsaturated ester, α -amidoacrylate ester	JACS 116 4062 (1994)
$[\text{Rh}(\text{NBD})(\text{diPAMP})]\text{BF}_4$	α -amidoacrylamide	TL 35 5785 (1994)
$[\text{Rh}(\text{NBD})(\text{Ph-CAPP})]\text{BF}_4$	α -amidoacrylamide	TL 35 5785 (1994)
 $[\text{Rh}(\text{COD})\left(\begin{array}{c} \text{R} \quad \text{R} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{P} \quad \text{P} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{R} \quad \text{R} \end{array}\right)]\text{OTf}$ <p>(R = Me, Et, Pr, <i>i</i>-Pr)</p>	α -amidoacrylate esters, enol acetates	JACS 113 8518 (1991); 115 10125 (1993); 116 10847 (1994); 117 9375 (1995)
 $[\text{Rh}(\text{COD})\left(\begin{array}{c} \text{Me} \quad \text{Me} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{P} \quad \text{P} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{Me} \quad \text{Me} \end{array}\right)]\text{OTf}$	α -amidoacrylate ester	JACS 117 9375 (1995)

$\left[\text{Rh}(\text{COD}) \left(\begin{array}{c} \text{R} \\ \diagup \\ \text{PC}_3\text{H}_4\text{FeC}_3\text{H}_4\text{P} \\ \diagdown \\ \text{R} \end{array} \right) \right] \text{OTf}$ <p>(R = Me, Et)</p>	α -amidoacrylate ester, α,β -unsaturated ester	TL 35 9363 (1994)
$[\text{Rh}(\text{COD})(\text{anthraphos})]\text{BF}_4$	α -amidoacrylic acid	TL 35 7593 (1994)
$[\text{Rh}(\text{COD})(o\text{-EtC}_6\text{H}_4\text{PPhCH}_2\text{CH}_2\text{PPh-C}_6\text{H}_4\text{Et-}o)]\text{BF}_4$	α -amidoacrylic acids and esters	TL 36 8271 (1995)
$[\text{Rh}(\text{COD})_2]\text{BF}_4$, $\text{R}_2\text{PCHMeFer-FerCH-MePR}_2$	α -amidoacrylate esters	JACS 117 9602 (1995)
$[\text{Rh}(\text{COD})_2]\text{ClO}_4$, 	α -amidoacrylic acid	SL 49 (1991)
$[\text{Rh}(\text{COD})\text{Cl}]_2$, 	acrylic acid	SL 155 (1993)
$\left[(\text{COD})\text{Rh} \left(\begin{array}{c} \text{Ph}_2\text{P} \\ \diagup \\ \text{P} \\ \diagdown \\ \text{Ph}_2\text{P} \end{array} \right) \text{NCONHPh} \right] \text{BF}_4$	acrylic acid	SL 155 (1993)
$[\text{RhL}(\text{COD})]\text{SbF}_6$ (L = glucose 3,4-diphosphinites)	α -amidoacrylic acids and esters	JACS 116 4101 (1994)
$\text{Rh}(\text{O}_2\text{CCF}_3)_2$ (tolbinap)	enamides	TL 28 4829 (1987)
chiral (aminoalkyl)ferrocenylphosphine-Rh	trisubstituted acrylic acids	JACS 109 7876 (1987) TL 29 5969 (1988)
chiral pyrrolidinodiphosphines-Rh	itaconic acid; α,β -unsaturated acids, esters, and ketones; α -amidoacrylic acids	CL 567 (1978) Ber 119 3326 (1986) Angew Int 27 1180 (1988) Syn 743 (1989) JOMC 387 209 (1990) TL 32 3671 (1991) JACS 115 152 (1993)
diop-Rh	α,β -unsaturated carboxylic acids, α -amidoacrylic acids and esters	CC 481 (1971) JACS 94 6429 (1972) JOC 56 1783 (1991)
$\text{Ar}_2\text{PCH}_2\text{CH}(\text{O})\text{CH}(\text{O})\text{CH}_2\text{PAr}_2\text{-Rh}$	α,β -unsaturated ester	TL 29 4755 (1988); 30 735 (1989); 31 261 (1990) JOC 60 4339 (1995)
	α -amidoacrylic acid and ester	TL 35 6071 (1994)

Catalyst	Substrate	
$\text{Ph}_2\text{PCH}(\text{CH}_2\text{OR})\text{CH}_2\text{PPh}_2\text{-Rh}$	α -amidoacrylic acids and esters	J Chem Res (S) 117 (1982)
$o\text{-Ph}(\text{Me})\text{PC}_6\text{H}_4\text{P}(\text{Me})\text{Ph-Rh(I)}$	α -amidoacrylate ester	JACS 115 4040 (1993)
$\{R,R\text{-1,2-bis}[(\text{phenyl-}o\text{-anisoyl})\text{-phosphino-ethane}]\text{-Rh(I)}$	various α -amidoacrylate derivatives	JACS 99 5946 (1977); 109 1746 (1987); 115 4040 (1993)
organosamarium compound	alkenes	JACS 114 2761 (1992)

3.2. Diimide Reduction ($\text{HN}=\text{NH}$)

J Chem Ed 42 254 (1965) (review)

Angew Int 4 271 (1965) (review)

Syn Commun 12 287 (1982) (HONH_2 , EtOAc)

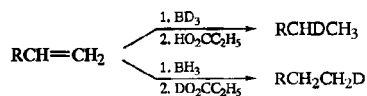
JOC 52 4665 (1987); 57 6092 (1992) (both TsNHNH_2 , NaOAc); 59 4345 (1994) (N_2H_4 , NaIO_4)

JACS 110 1529 (1988) (N_2H_4 , air, CuSO_4)

Org Rxn 40 91 (1991) (review)

TL 34 4137 (1993) $\left(\begin{array}{c} \text{O} \quad \text{S} \quad \text{O} \\ \diagdown \quad \diagup \\ \text{HN-NH} \end{array} \right), h\nu$

3.3. Hydroboration-Protonolysis



JACS 81 4108 (1959)

JOMC 255 135 (1983)

3.4. Metal Hydrides

LiH , VCl_3 ($\text{RCH}=\text{CH}_2$ only)

JOC 45 1041 (1980)

NaH , $\text{NaO-}i\text{-Bu}$, FeCl_3

TL 3947 (1977)

NaH , $\text{NaO-}i\text{-Am}$, $\text{Ni}(\text{OAc})_2$

TL 1069 (1977)

NaBH_4 , CoCl_2

JACS 108 67 (1986)

NaBH_4 , cat $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$

JACS 104 5781 (1982)

JOC 56 1192 (1991)

NaBH_3CN , HCl

JACS 113 5775 (1991)

LiAlH_4

TL 31 553 (1990)

LiAlH_4 , TiCl_4 or ZrCl_4

TL 15 (1976)

JOMC 142 71 (1977)

LiAlH_4 , CoCl_2	JOC 43 2567 (1978)
LiAlH_4 , NiCl_2	TL 4481 (1977)
R_3SiH , $\text{CF}_3\text{CO}_2\text{H}$	Tetr 23 2235 (1967) Syn 633 (1974) Org Prep Proc Int 12 13 (1980) JACS 108 1239 (1986) TL 36 7949 (1995) (enamide)
Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$, NH_4F	SL 647 (1992)
$(\text{EtO})_3\text{SiH}$, cat $\text{Pd}(\text{OAc})_2$, H_2O	TL 31 4719 (1990) JOC 55 3452 (1990)
R_3SnH , cat $(p\text{-BrC}_6\text{H}_4)_3\text{NSbCl}_6$ ($\text{Ar}_2\text{C}=\text{CH}_2$; 1,3-diene)	JACS 114 5457 (1992); 115 6072 (1993)
$\text{HM}(\text{CO})_5\text{Cp}$ ($\text{M} = \text{Mo}, \text{W}$), $\text{HOs}(\text{CO})_2\text{Cp}$, $\text{HRe}(\text{CO})_5$ or $\text{HMn}(\text{CO})_5$; TfOH	JACS 116 8602 (1994)
LaNi_5H_6	CC 163 (1984)

3.5. Miscellaneous Reagents

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 3.3, p 471

Li , NH_3	JACS 111 1007 (1989)
Na , $t\text{-BuOH}$, amide	JOC 44 2369 (1979)
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, Na_2CO_3 , cat Pd-C , H_2O	JOC 50 3408 (1985)
Mg , MeOH ($\text{ArCH}=\text{CHAr}$ only)	JOC 44 3972 (1979) TL 30 55 (1988)
Zn , HCl ($\text{ArCH}=\text{CHAr}$)	JACS 115 5843 (1993)
Zn , cat NiCl_2 , D_2O , dioxane (allylic alcohol)	JOC 55 1664 (1990)
<i>Saccharomyces cerevisiae</i> (allylic alcohols, enantioselective)	Bioorg Chem 10 22 (1981) Experientia 38 775 (1982)
Pd black, HCO_2H	TL 29 5599 (1988)

3.6. Conjugate Reduction

See also page 8, Section 3.1.2.



$\text{X} = \text{Ar}$

Li , cat $(4\text{-}t\text{-BuC}_6\text{H}_4)_2$, ultrasound	TL 30 4931 (1989)
Me_2SiCl , NaI , PhCO_2H	TL 30 4741 (1989)

$\text{X} = \text{CHO}$

H_2 , CO , cat $\text{Co}_2(\text{CO})_8$	Compt Rend C 281 877 (1975)
H_2 , cat $\text{Rh-Al}_2\text{O}_3$	Compt Rend C 284 577 (1977)

H_2 , cat $ClRh(PPh_3)_3$	JCS C 270 (1967) JOC 34 3684 (1969)
H_2 ; cat $HRhCO(PPh_3)_3$, $Rh_4(CO)_{12}$ or $Rh_6(CO)_{16}$; cat diphosphine (chiral)	J Mol Catal 16 51 (1982)
H_2 , cat Ni_2B	TL 35 5595 (1994)
H_2 , $NaBH_4$ -cat $Ni(OAc)_2$ or $PdCl_2$	JOC 42 551 (1977)
H_2 , cat $PdCl_2$ -ferrocenylamine sulfide	TL 32 5489 (1991)
H_2 , cat $[(t-Bu_2PH)PdP(t-Bu)_2]_2-O_2$	TL 34 59 (1993)
H_2 or Et_3SiH or Me_2SiClH , cat $Pd(hfacac)_2-Me_3Si(OSiHMe)_nOSiMe_3$	TL 34 3075 (1993)
$(NH_4)_2O_2CH$, cat $Pd-C$	TL 35 8649 (1994)
$(Et_3NH)_2O_2CH$, cat $Pd-C$	JOC 43 3985 (1978)
Al , $NiCl_2 \cdot 6H_2O$	TL 30 6567 (1989)
$i-Bu_2AlH$, HMPA	JOC 51 537 (1986)
Et_3SiH , cat $ClRh(PPh_3)_3/K_2CO_3$	TL 5035 (1972) Organomet 1 1391 (1982)
Ph_2SiH_2 , cat $Pd(PPh_3)_4$, cat $ZnCl_2$	JACS 108 7314 (1986)
Ph_2SiH_2 , cat $Pd(dppe)_2$, cat $ZnCl_2$	TL 30 4295 (1989)
$Me_3Si(OSiHMe)_nOSiMe_3$, cat $RhCl_3$, cat $[(n-C_8H_{17})_3NCH_3]Cl$	J Mol Catal 37 359 (1986)
$n-Bu_3SnH$, cat $Pd(PPh_3)_4$	TL 23 477 (1982)
$n-Bu_3SnH$, cat $Pd(PPh_3)_4$, $HOAc$	TL 23 1825 (1982)
$n-Bu_3SnH$, CuI , $LiCl$	SL 64 (1989)
$NaHFe_2(CO)_8$	JACS 100 1119 (1978)
$HCo(CO)_4$	JOC 27 3698 (1962) JACS 85 2782 (1963)
$LaNi_5H_6$	CC 163 (1984)
$LiHCu \equiv C(CH_2)_2CH_3$	JACS 96 1623 (1974)
$[HCu(PPh_3)]_6$, H_2O	JACS 116 2151 (1994)
$[HCu(PPh_3)]_6$, Me_3SiCl/H_3O^+ or $n-Bu_4NF-H_2O$	TL 30 5677 (1989)
$Fe(CO)_5$, $NaOH$	JOC 37 1542 (1972) Syn 596 (1976)
CO , H_2O , cat $Rh_6(CO)_{16}$	CL 379 (1973)
Li , NH_3	Org Rxs 23 1 (1976) JOC 46 5371 (1981)
$Na_2S_2O_4$, $NaHCO_3$, cat Aliquat [®]	TL 26 831 (1985)
$Na_2S_2O_4$, $RCHO$ or R_2CO	TL 36 1107 (1995)
$NaTeH$	CL 847 (1980)

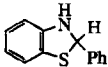
X = COR

electrolysis	JOC 52 276 (1987)
Li, NH ₃ (Birch reduction)	JCS 3045 (1954) Org Rxs 23 1 (1976) (review) JACS 108 4561 (1986) JOC 57 4590 (1992)
Li·4NH ₃	JOC 43 4647 (1978)
Li or Na, HMPA or NH ₃	JACS 92 2800 (1970)
Li, NH ₃ , EtOH	JACS 86 1761 (1964)
Li, NH ₃ , <i>t</i> -BuOH	JOC 32 2851 (1967); 42 183 (1977); 50 2607 (1985); 52 2263, 3346 (1987); 57 4005 (1992) JACS 106 3539 (1984); 111 6287 (1989); 114 7375 (1992)
Li, EtNH ₂ , <i>t</i> -BuOH	Syn 400 (1980)
Na, HMPA, (ROH)	JACS 92 2783 (1970)
C ₈ K, HN(SiMe ₃) ₂	Syn 30 (1979)
Mg, MeOH	TL 32 4183 (1991)
Mg, TiCl ₄ , <i>t</i> -BuOH	TL 27 4153 (1986)
Al, NiCl ₂ ·6H ₂ O	TL 30 6567 (1989)
TiCl ₃ , MeOH, NH ₃	Helv 13 1308 (1930)
Zn, HCl	Quart Rev 23 522 (1969)
Zn, HOAc (RCOCH=CHCOR)	TL 35 4819 (1994)
Zn, cat cyanocob(I)alamin, HOAc, H ₂ O	Helv 62 2361 (1979)
Zn, cob(I)alamin, HOAc	Helv 62 2361 (1979)
Zn, NiCl ₂ , H ₂ O, CH ₃ OCH ₂ CH ₂ OH, ultrasound	TL 28 2347 (1987)
Zn, NiCl ₂ , H ₂ O, CH ₃ OCH ₂ CH ₂ OH, NH ₃ -NH ₄ Cl or Et ₃ N, ultrasound	TL 28 2351 (1987) JOC 60 7837 (1995)
Zn, cat NiCl ₂ , D ₂ O, dioxane	JOC 55 1664 (1990)
Yb, NH ₃	JOC 43 4555 (1978)
H ₂ , cat Et ₄ N[HCr ₂ (CO) ₁₀]	TL 32 1199 (1991)
H ₂ , cat HRuCIL ₄ or H ₂ RuL ₄ (chiral ligands)	TL 27 5497 (1986) (chiral)
H ₂ , cat H ₂ Ru(PPh ₃) ₄ or RuCl ₂ (PPh ₃) ₃ , glycoside	TL 4083 (1976) (chiral)
H ₂ , CO, cat Co ₂ (CO) ₈	Compt Rend 281 877 (1975)
H ₂ , cat Co ₂ (CO) ₈ (PR ₃)	JOMC 284 101 (1985) (chiral)
H ₂ , cat K ₃ Co(CN) ₅ H	TL 115 (1979) JOC 45 3860 (1980)
H ₂ , cat bis(dimethylglyoximate)cobalt(II)-quinine	CL 265 (1973) (chiral)

H ₂ , cat Rh-C, Na ₂ CO ₃	JOC 50 2438 (1985); 54 3988 (1989)
H ₂ , cat Rh-Al ₂ O ₃	Compt Rend C 284 577 (1977) JACS 111 6257 (1989)
H ₂ , cat ClRh(PPh ₃) ₃	JACS 88 4537 (1966); 107 8066 (1985) JCS C 1894 (1966) JOC 34 3684 (1969)
H ₂ , cat [Rh(COD)(<i>i</i> -Pr ₂ PC ₃ H ₄ FeC ₃ H ₄ P- <i>i</i> -Pr ₂)]OTf	TL 35 4963 (1994)
H ₂ , cat [Rh(diolefin)L ₂]BF ₄ (L = chiral phosphine)	JOC 43 1787 (1978) (chiral)
H ₂ , cat RhCl ₃ ·3H ₂ O, cat [(<i>n</i> -C ₈ H ₁₇) ₃ NCH ₃]Cl	J Mol Catal 34 229 (1986) TL 28 1321 (1987)
H ₂ , cat HRh(PPh ₃) ₄ , PhCHOHCH ₃	Can J Chem 57 218 (1979)
H ₂ , cat [Ir(COD)(py)(PCy ₃)]PF ₆	TL 22 303 (1981)
H ₂ , Raney Ni	SL 191 (1993)
H ₂ , cat Ni ₂ B	TL 35 5595 (1994)
H ₂ , cat NaH-NaO- <i>t</i> -Am-Ni(OAc) ₂	JOC 45 1946 (1980)
H ₂ , cat Pd-C	JOC 23 1853 (1958); 52 2875, 5594 (1987) JACS 107 7967 (1985); 108 4561 (1986)
H ₂ , cat Pd(OH) ₂ -C	JOC 54 3738 (1989)
H ₂ , cat PdCl ₂ -ferrocenylamine sulfide	TL 32 5489 (1991)
H ₂ , cat [(<i>t</i> -Bu ₂ PH)PdP(<i>t</i> -Bu) ₂] ₂ -O ₂	TL 34 59 (1993)
H ₂ or Et ₃ SiH or Me ₂ SiClH, cat Pd(hfacac) ₂ -Me ₃ Si(OSiHMe) _n OSiMe ₃	TL 34 3075 (1993)
H ₂ , cat PtO ₂	JOC 23 1853 (1958) JACS 108 7967 (1985)
H ₂ , cat Cu-Al ₂ O ₃	JOC 56 4329 (1991)
H ₂ , cat [HCu(PPh ₃)] ₆	JACS 111 8818 (1989)
LiH, <i>t</i> -BuOH, Ni(OAc) ₂	TL 36 6051 (1995)
NaH, NaO- <i>t</i> -Am, Ni(OAc) ₂ , (MgBr ₂)	JOC 44 2203 (1979)
NaH, <i>t</i> -AmOH, Ni(OAc) ₂ , (Me ₃ SiCl)	TL 27 5487 (1986)
HBI ₂	TL 3865 (1976)
CB	JOC 55 5678 (1990) SL 349 (1991)
CB, cat ClRh(PPh ₃) ₃	JOC 55 5678 (1990)
9-BBN	SL 349 (1991)
NaBH ₄	JCS C 616 (1968)
NaBH ₄ , diglyme, amine base	JCS 5280 (1965)
NaBH ₄ , CoCl ₂ ·6H ₂ O	JOC 55 4497 (1990)

NaBH ₄ , cat NiCl ₂ ·6H ₂ O	JACS 111 6247 (1989)
LiHB(sec-Bu) ₃	JACS 109 6389 (1987); 112 6690 (1990)
KHB(sec-Bu) ₃	JOC 40 146 (1975); 41 2194 (1976)
KHBPh ₃	JOC 52 5564 (1987) Syn Commun 18 89 (1988)
NaBH ₃ CN, ZnCl ₂	JOC 50 1927 (1985)
MAD/LiHBEt ₃	TL 30 5053 (1989)
MAD/LiHB(sec-Bu) ₃	TL 30 5053 (1989); 31 6125 (1990)
BF ₃ ·OEt ₂ /LiHBEt ₃	TL 30 5053 (1989)
<i>i</i> -Bu ₂ AlH	JACS 110 3702 (1988) (4-hydroxy-2-alkenones)
<i>i</i> -Bu ₂ AlH, HMPA	JOC 51 537 (1986)
<i>i</i> -Bu ₂ AlH, cat MeCu, HMPA	JOC 51 537 (1986); 58 885 (1994) Syn Commun 16 639 (1986)
<i>i</i> -Bu ₂ AlH, <i>t</i> -BuCu, HMPA	JOC 53 5534 (1988)
<i>i</i> -Bu ₃ Al, cat Ni(mesal) ₂	JOC 47 4640 (1982)
HAL(OR) ₂ (R = <i>t</i> -Bu, <i>i</i> -Pr)	TL 3865 (1976)
HAL[N(<i>i</i> -Pr) ₂] ₂	TL 3865 (1976)
LiAlH ₄	JACS 110 3702 (1988) (4-hydroxy-2-alkenones) TL 30 127 (1989)
LiAlH ₄ , 4CuI	TL 4453 (1975) JOC 41 1939 (1976)
LiAlH ₄ , cat CuI, HMPA	CC 1013 (1980)
LiAlH ₄ , 2,4,6-Me ₃ C ₆ H ₂ Cu	JOC 46 192 (1981)
LiAl(O- <i>t</i> -Bu) ₃	JOC 35 2971 (1970)
LiAl(SR) ₃ (R = Me, <i>t</i> -Bu)	TL 2397 (1974)
LiAl(OMe) ₃ , CuBr	JOC 40 3619 (1975); 42 3180 (1977) CL 1007 (1987) TL 32 4453 (1991)
BF ₃ ·OEt ₂ /LiH ₂ Al(OMe) ₂ , CuBr	TL 30 5053 (1989)
NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂ , CuBr	JOC 40 3619 (1975); 42 3180 (1977); 57 3359 (1990)
PhSiH ₃ , cat Mo(CO) ₆ /H ₂ O	JOC 52 2576 (1987)
PhSiH ₃ or Ph ₂ SiH ₂ , cat M(CO) ₂ (enone) ₂ (M = Mo, W)	TL 35 3513 (1994)
Ph ₂ SiH ₂ , cat Pd(PPh ₃) ₄ , cat ZnCl ₂	TL 26 1353 (1985) JACS 108 7314 (1986)
R ₃ SiH (R = Me, Et), TiCl ₄ /H ₂ O	Chem Pharm Bull 25 1468 (1977)
R ₃ SiH, cat TiCl ₄ or ClRh(PPh ₃) ₃	TL 29 6199 (1988)

Et_3SiH , cat $\text{ClRh}(\text{PPh}_3)_3$	TL 5035 (1972) IACS 102 6602 (1980); 105 7538 (1983); 107 3731 (1985); 108 4586 (1986) Organomet 1 1390 (1982)
Et_3SiH , $n\text{-Pr}_3\text{SiH}$, $\text{Et}_2\text{Si}(\text{OEt})\text{H}$ or $(\text{Me}_2\text{SiH})_2\text{O}$; cat $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$	Chem Pharm Bull 20 1827 (1972)
RMe_2SiH ($\text{R} = \text{Me}, \text{Ph}$), cat $\text{RhH}_2[\text{PhCH}_2\text{P}(\text{Me})\text{Ph}]_2\text{ClO}_4$ or $[\text{RhCl}(\text{C}_6\text{H}_{10})]_2$ plus diop/ H_2O (chiral)	TL 3 (1975)
X_3SiH ($\text{X} = \text{Ph}, \text{OEt}$), cat Rh -diop	IOC 53 3057 (1988)
$(\text{EtO})_3\text{SiH}$, cat $\text{Pd}(\text{OAc})_2$	IOC 55 3452 (1990)
$\text{Me}_3\text{Si}(\text{OSiHMe})_n\text{OSiMe}_3$, cat RhCl_3 , cat $[(n\text{-C}_8\text{H}_{17})_3\text{NCH}_3]\text{Cl}$	J Mol Catal 37 359 (1986)
Ph_2SnH_2	TL 2221 (1966)
Ph_3SnH	Compt Rend 260 581 (1965) TL 2221 (1966) BSCF 1928 (1967) Chem Pharm Bull 16 1158 (1968); 18 453 (1970) Helv 56 1062 (1973)
$n\text{-Bu}_3\text{SnH}$	Ann 1996 (1983) TL 28 1313 (1987) IOC 56 3352 (1991)
$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{PPh}_3)_4$	TL 23 477 (1982); 30 5799 (1989); 34 7137 (1993)
$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{PPh}_3)_4$, ZnCl_2	TL 23 1825 (1982) Nouv J Chim 8 611 (1984)
$n\text{-Bu}_3\text{SnH}$, cat $\text{PdCl}_2(\text{PPh}_3)_2$, cat $n\text{-Bu}_3\text{SnOTf}$	Nouv J Chim 8 611 (1984)
$n\text{-Bu}_3\text{SnH}$, CuI , LiCl	SL 64 (1989)
LiSeH	IOC 56 6720 (1991)
NaSeH	IOC 56 6720 (1991)
NaTeH	CL 847 (1980) TL 27 3411 (1986) IOC 57 5596 (1992); 59 3500 (1994)
$\text{MHCr}_2(\text{CO})_{10}$ ($\text{M} = \text{Na}, \text{K}$)	Syn 596 (1976)
$\text{MHFe}(\text{CO})_4$ ($\text{M} = \text{Na}, \text{K}$)	IOC 37 1542 (1972) JCS Perkin I 1273 (1975) Syn 596 (1976) Tetr 38 3447 (1982) TL 31 3859 (1990)
$\text{NaHFe}_2(\text{CO})_8$, HOAc	IACS 100 1119 (1978)
$(\text{Et}_4\text{N})\text{HFe}_3(\text{CO})_{11}$	JOMC 171 85 (1979)

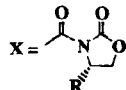
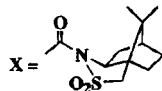
HCo(CO)_4	JACS 85 2782 (1963)
LaNi_5H_6	CC 163 (1984) JOC 52 5695 (1987)
$[\text{HCu(PPh}_3)_6]$	JACS 110 291 (1988)
$[\text{HCu(PPh}_3)_6], \text{H}_2\text{O}$	JACS 110 291 (1988) TL 31 3237 (1990)
$\text{LiHCu}(n\text{-Bu})$	JACS 96 3686 (1974)
$\text{LiHCuC}\equiv\text{C(CH}_2)_2\text{CH}_3$	JACS 96 1623 (1974)
Li_2CuH_3	JOC 43 183 (1978)
KO_2CH , cat Pd(OAc)_2	SL 27 (1991)
$(\text{NH}_4)_2\text{O}_2\text{CH}$, cat Pd-C	TL 35 171, 8649 (1994)
$(\text{R}_3\text{NH})\text{O}_2\text{CH}$ (R = Et, <i>n</i> -Bu), cat Pd-C	JOC 43 3985 (1978)
Fe(CO)_5 , NaOH	JOC 37 1542 (1972)
$\text{Na}_2\text{Fe(CO)}_4$, Fe(CO)_5 , HOAc	Acct Chem Res 8 342 (1975)
CO , H_2O , cat $\text{Rh}_6(\text{CO})_{16}$	CL 379 (1973)
CO , cat $\text{Rh}_4(\text{CO})_{12}$ -resin	CL 203 (1975)
benzylic alcohol, cat $\text{RuCl}_2(\text{PPh}_3)_3$	JOC 40 1887 (1975)
$\text{Na}_2\text{S}_2\text{O}_4$, RCHO or R_2CO	TL 36 1107 (1995)
$\text{Na}_2\text{S}_2\text{O}_4$, NaHCO_3 , Adogen 464 [®] , H_2O , benzene	Tetr 42 4603 (1986) TL 36 5379 (1995)
$\text{Na}_2\text{S}_2\text{O}_4$, NaHCO_3 , cat Aliquat [®]	TL 26 831 (1985)
 , AlCl_3 , CH_3OH	Syn 308 (1984)
$\text{PhCH}_2\text{NH}_2/\text{KO}-t\text{-Bu}/\text{H}_3\text{O}^+$	JACS 89 2794 (1967)
baker's yeast	CL 587 (1984) TL 27 4737 (1986) (α -chloro enones, chiral)
<i>Beauveria sulfurescens</i>	JOC 47 792 (1982) (enantiospecific); 52 4893 (1987) (enantiospecific)
$\text{X} = \text{CO}_2\text{H}$	
Li, NH_3	Org Rxs 23 1 (1976) JOC 54 1483 (1989)
Na, NH_3 , <i>t</i> -BuOH	TL 27 3923 (1986)
$\text{C}_8\text{K}/\text{H}_3\text{O}^+$	Syn 30 (1979)
TiCl_3 , MeOH, NH_3	Helv 13 1308 (1930)
CrSO_4 , H_2O	JACS 88 4964 (1966)

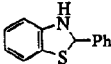
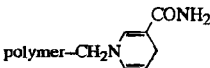
cob(I)alamin, Zn, HOAc	Helv 62 2361 (1979)
Sm, I ₂ , ROH	SL 443 (1995)
SmI ₂ , CH ₃ OH	JACS 102 2693 (1980)
SmI ₂ , HMPA, THF	TL 33 5007 (1992)
H ₂ , cat RuCl ₂	JACS 88 5150 (1966)
H ₂ , cat Ru(OAc) ₂ (BINAP)	JOC 52 3174 (1987) (chiral) JACS 113 589 (1991)
H ₂ , cat ClRh(PPh ₃) ₃	JOC 34 3684 (1969)
H ₂ , cat Rh(I), chiral ligand	CC 481 (1971) JACS 99 5946 (1977)
H ₂ , cat RhCl ₃	TL 29 1759 (1988)
H ₂ , cat [RhCl(1,5-hexadiene)] ₂	TL 29 1759 (1988)
HCO ₂ H, Et ₃ N, cat Rh, chiral ligand	Angew Int 27 1180 (1988) Syn 743 (1989) JOMC 387 209 (1990) JACS 115 152 (1993)
H ₂ , cat Raney Ni-NaBr-tartaric acid	JOC 52 1139 (1987) (chiral)
H ₂ , cat Pd-C	JOC 54 4218 (1989)
HCO ₂ H, cat Pd black	TL 29 5599 (1988)
(NH ₄)O ₂ CH, cat Pd-C	TL 35 8651 (1994)
(EtO) ₃ SiH, cat Pd(OAc) ₂ , H ₂ O	TL 31 4719 (1990)
PhSiH ₃ , cat Mo(CO) ₆ /H ₂ O	JOC 52 2576 (1987)
LiSeH	JOC 56 6720 (1991)
NaTeH	Syn 545 (1978)
cat [RuH(BINAP) ₂]PF ₆ , ROH (chiral)	TL 33 5783 (1992)
HCo(CN) ₅ ³⁻	Catal Rev 1 37 (1967) (review)
HCo(CN) ₅ ³⁻ , β-cyclodextrin	TL 31 1941 (1990)
HONH ₂ , EtOAc	Syn Commun 12 287 (1982)
X = CO₂Na	
H ₂ , cat Raney Ni-NaBr-tartaric acid	JOC 52 1139 (1987) (chiral)
X = CO₂R	
Mg, CH ₃ OH	CL 633 (1983) (lactone) TL 27 2409 (1986); 28 5287 (1987); 29 5505 (1988) JOC 52 4641 (1987); 58 6349, 6486 (1993); 59 3433, 5414 (1994) JACS 111 2599 (1989)

Mg, CH ₃ OH, ultrasound	CC 344 (1986)
cob(T)alamin, Zn, HOAc	Helv 62 48, 2361 (1979)
CrSO ₄ , H ₂ O	JACS 88 4964 (1966) Org Syn Coll Vol 5 993 (1973)
Zn, cat NiCl ₂ , H ₂ O, dioxane, (ultrasound)	JOC 54 5313 (1989); 55 1664 (1990)
Zn, NiCl ₂ , H ₂ O, CH ₃ OCH ₂ CH ₂ OH, ultrasound	TL 28 2347 (1987)
Sm, I ₂ , ROH	SL 443 (1995)
SmI ₂ , CH ₃ OH	JACS 102 2693 (1980) TL 36 3099 (1995)
SmI ₂ , H ₂ O, THF	JOC 58 5008 (1993)
SmI ₂ , HMPA, THF	TL 33 5007 (1992)
H ₂ , cat bis(dimethylglyoximate)cobalt(II)-quinine	CL 265 (1973) (chiral)
H ₂ , cat Rh-Al ₂ O ₃	TL 29 3171 (1988) JOC 58 6486 (1993)
H ₂ , cat RhCl ₃ ·3H ₂ O, cat [(n-C ₈ H ₁₇) ₃ NCH ₃]Cl	TL 28 1321 (1987)
H ₂ , cat ClRh(PPh ₃) ₃	JACS 90 1673 (1968) Discuss Faraday Soc 46 60 (1968) JOC 34 3684 (1969)
H ₂ , cat [Rh(NBD)(dppb)]BF ₄	JACS 108 2476 (1986)
H ₂ , cat [Rh(NBD)(BINAP)]BF ₄	JACS 108 2476 (1986) (chiral)
H ₂ , Raney Ni	Tetr 44 6889 (1988)
H ₂ , cat Pd-C	JOC 52 4603 (1987) (lactone); 54 3226 (1989) SL 537 (1992) TL 35 7417 (1994)
H ₂ , cat Pd-C, ultrasound	JOC 54 5630 (1989)
H ₂ , cat PdCl ₂	JACS 91 2579 (1969)
H ₂ , cat PdCl ₂ -ferrocenylamine sulfide	TL 32 5489 (1991)
H ₂ or Et ₃ SiH, cat Pd(hfacac) ₂ -Me ₃ Si(OSiHMe) _n OSiMe ₃	TL 34 3075 (1993)
H ₂ , cat Pt-C	JOC 59 394 (1994)
H ₂ , cat PtO ₂	JOC 52 4641 (1987)
CB, cat ClRh(PPh ₃) ₃	JOC 55 5678 (1990)
LiBH ₄ , cat NiCl ₂	SL 743 (1990)
NaBH ₄	JOC 31 620 (1966)
NaBH ₄ , CF ₃ CH ₂ OH, EtOH	JOC 50 3948 (1985)

NaBH ₄ , cat CoCl ₂ ·6H ₂ O	Chem Pharm Bull 19 817 (1971)
NaBH ₄ , cat NiCl ₂ ·6H ₂ O	Chem Pharm Bull 19 817 (1971) JACS 106 5585 (1984) (lactone) TL 28 4037 (1987) (lactone); 29 3829 (1988) JOC 60 7927 (1995) SL 1221 (1995)
NaBH ₄ , Cu ₂ Cl ₂	JOC 54 5308 (1989)
NaBH ₄ , cat CuCl ₂ ·2H ₂ O	Chem Pharm Bull 19 817 (1971)
borohydride exchange resin, CuSO ₄	SL 726 (1995)
LiHB(<i>sec</i> -Bu) ₃ , <i>t</i> -BuOH	JOC 40 2846 (1975); 41 2194 (1976)
KHBPh ₃ , PhOH	Bull Korean Chem Soc 9 352 (1988)
<i>i</i> -Bu ₂ AlH, cat MeCu, HMPA	JOC 51 537 (1986); 53 4877 (1988)
LiAlH ₄ , CuI	CC 1013 (1980)
NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂ , CuBr	JOC 40 3619 (1975); 42 3180 (1977); 55 6236 (1990); 58 3840 (1993) JACS 109 5432 (1987)
LiHAl(OMe) ₃ , CuBr	JOC 42 3180 (1977)
PhSiH ₃ , cat Mo(CO) ₆ /H ₂ O	JOC 52 2576 (1987)
Ph ₂ SiH ₂ , cat Pd(PPh ₃) ₄ , cat ZnCl ₂	JACS 108 7314 (1986)
Et ₃ SiH, cat ClRh(PPh ₃) ₃ /H ₃ O ⁺	Chem Pharm Bull 22 2767 (1974) Syn Commun 15 965 (1985) JACS 109 5432 (1987) JOC 52 4414 (1987)
(EtO) ₃ SiH, cat Pd(OAc) ₂	JOC 55 3452 (1990)
Me ₃ Si(OSiHMe) ₄ OSiMe ₃ , cat RhCl ₃ , cat [(<i>n</i> -C ₈ H ₁₇) ₃ NCH ₃]Cl	J Mol Catal 37 359 (1986)
PhSH, Et ₃ N/ <i>n</i> -Bu ₃ SnH	SL 825 (1991)
NaSeH	JOC 56 6720 (1991)
NaTeH	Syn 545 (1978); 847 (1980) JOC 59 3500 (1994)
KHCr ₂ (CO) ₁₀	Syn 596 (1976)
NaHFe ₂ (CO) ₈	JACS 100 1119 (1978)
(Et ₄ N)HFe ₃ (CO) ₁₁	JOMC 171 85 (1979)
HCo(CN) ₅ ³⁻	Catal Rev 1 37 (1967) (review)
HCo(CN) ₅ ³⁻ , β -cyclodextrin	TL 31 1941 (1990)
LaNi ₅ H ₆	CC 163 (1984) JOC 52 5695 (1987)
LaNi _{4.5} Al _{0.5} H ₅	JOC 52 5695 (1987)

$[\text{HCu}(\text{PPh}_3)]_6, \text{H}_2\text{O}$	JACS 110 291 (1988)
$\text{LiHCu}\equiv\text{C}(\text{CH}_2)_2\text{CH}_3$	JACS 96 1623 (1974)
KO_2CH , cat $\text{Pd}(\text{OAc})_2$	SL 27 (1991)
$(\text{NH}_4)_2\text{O}_2\text{CH}$, cat Pd-C	TL 35 8649 (1994)
$(\text{R}_3\text{NH})\text{O}_2\text{CH}$, cat Pd-C	JOC 43 3985 (1978)
HCO_2H , cat Pd black	TL 29 5599 (1988)
HCO_2H , Et_3N , cat Rh, chiral ligand	JOMC 387 209 (1990)
CO , H_2O , cat $\text{Rh}_6(\text{CO})_{16}$	CL 379 (1973)
CO , cat $\text{Rh}_4(\text{CO})_{12}$ -resin	CL 203 (1975)
$\text{Fe}(\text{CO})_5$, NaOH	JOC 37 1542 (1972)
$\text{Na}_2\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, HOAc	JACS 100 1119 (1978)
baker's yeast	TL 28 1447 (1987) (enantioselective on methyl 2,4,4-trichloro-2-butenates); 33 6375 (1992) (lactone) JOC 54 4989 (1989) (enantioselective, 2-chloro- 2-alkenoate esters)
X = CONR₂	
Mg, CH_3OH	TL 21 2915 (1980) JCS Perkin I 2912 (1981); 1781 (1985) JOC 49 4138 (1984)
TiCl_3 , CH_3OH , NH_3	Helv 13 1308 (1930)
cob(I)alamin, Zn, HOAc	Helv 62 2361 (1979)
H_2 , cat $\text{RuCl}_2(\text{BINAP})\cdot\text{Et}_3\text{N}$	TL 36 7379 (1995)
H_2 , cat nickel boride	JOC 37 3552 (1972)
H_2 , cat PdCl_2 -ferrocenylamine sulfide	TL 32 5489 (1991)
CB, cat $\text{CIRh}(\text{PPh}_3)_3$	JOC 55 5678 (1990)
NaBH_4	JOC 31 620 (1966)
borohydride exchange resin, CuSO_4	SL 726 (1995)
KHBPh_3 , PhOH	Bull Korean Chem Soc 9 352 (1988)
PhSiH_3 , cat $\text{Mo}(\text{CO})_6/\text{H}_2\text{O}$	JOC 52 2576 (1987)
Ph_2SiH_2 , cat $\text{Pd}(\text{PPh}_3)_4$, cat ZnCl_2	JACS 108 7314 (1986)
$(\text{EtO})_3\text{SiH}$, cat $\text{Pd}(\text{OAc})_2$, cat $\text{HC}\equiv\text{CCO}_2\text{Me}$, H_2O , THF	JOC 55 3452 (1990)
NaTeH	Syn 545 (1978)
$\text{NaHFe}_2(\text{CO})_8$	JACS 100 1119 (1978)

HCo(CN) ₅ ³⁻ , β-cyclodextrin	TL 31 1941 (1990)
CO, H ₂ O, cat Rh ₆ (CO) ₁₆	CL 379 (1973)
CO, cat Rh ₄ (CO) ₁₂ -resin	CL 203 (1975)
Sm, I ₂ , ROH	SL 443 (1995)
SmI ₂ , HMPA, THF	TL 33 5007 (1992)
 X =	
CB, cat ClRh(PPh ₃) ₃	IOC 55 5678 (1990)
 X =	
LiHB(sec-Bu) ₃	TL 27 4717 (1986)
X = CN	
Mg, CH ₃ OH	JOC 40 127 (1975); 41 1873 (1976); 48 4087 (1983); 50 5649 (1985); 51 449 (1986); 53 477 (1988) Tetr 32 2583 (1976); 40 757 (1984) JACS 99 1536 (1977); 105 7638 (1983); 115 11485 (1993) TL 3957 (1979); 29 147 (1988) SL 391 (1993)
CrSO ₄ , H ₂ O	JACS 88 4964 (1966)
H ₂ , cat ClRh(PPh ₃) ₃	Discuss Faraday Soc 46 60 (1968) IOC 34 3684 (1969)
H ₂ , cat PdCl ₂ -ferrocenylamine sulfide	TL 32 5489 (1991)
NaBH ₄	IOC 31 620 (1966); 53 2413 (1988); 59 7876 (1994) Can J Chem 56 41 (1978)
borohydride exchange resin, CuSO ₄	SL 726 (1995)
KHBPh ₃ , PhOH	Bull Korean Chem Soc 9 352 (1988)
NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂ , CuBr/sec-BuOH	IOC 45 167 (1980)
PhSiH ₃ , cat Mo(CO) ₆ /H ₂ O	IOC 52 2576 (1987)
Ph ₂ SiH ₂ , cat Pd(PPh ₃) ₄ , cat ZnCl ₂	JACS 108 7314 (1986)
NaTeH	SL 1189 (1995)
KHCr ₂ (CO) ₁₀	Syn 596 (1976)
NaHFe(CO) ₄	JCS Perkin I 1273 (1975)

$\text{NaHFc}_2(\text{CO})_8$	JACS 100 1119 (1978)
$\text{Fe}(\text{CO})_5$, NaOH	IOC 37 1542 (1972)
$\text{Na}_2\text{Fe}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, HOAc	JACS 100 1119 (1978)
$\text{HCo}(\text{CN})_5^{3-}$	Catal Rev 1 37 (1967) (review)
$\text{HCo}(\text{CN})_5^{3-}$, β -cyclodextrin	TL 31 1941 (1990)
CO , H_2O , cat $\text{Rh}_6(\text{CO})_{16}$	CL 379 (1973)
$(\text{R}_3\text{NH})\text{O}_2\text{CH}$, cat Pd-C	JOC 43 3985 (1978)
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, Na_2CO_3 , cat Pd-C, H_2O	JOC 50 3408 (1985)
X = NO₂	
H_2 , cat $\text{ClRh}(\text{PPh}_3)_3$	JCS C 1894 (1966) JOC 34 3684 (1969)
H_2 , cat $\text{Pd}_2\text{Cl}_2(\text{PhN}=\text{NPh})_2$	J Mol Catal 39 279 (1987)
LiBH_4	JACS 78 4984 (1956)
NaBH_4	JACS 78 4984 (1956); 108 1039 (1986) JOC 32 4134 (1967); 55 5766 (1990)
NaBH_4 , silica	TL 24 227 (1983)
LiHBR_3 (R = Et, s-Bu)	Syn Commun 14 1093 (1984)
$\text{Zn}(\text{BH}_4)_2$	TL 32 3579 (1991) Tetr 48 5317 (1992)
$\text{NaHB}(\text{OMe})_3$	JACS 78 4984 (1956)
LiAlH_4	JACS 78 4984 (1956)
$n\text{-Bu}_3\text{SnH}/\text{H}_2\text{F}_2$, MeOH	TL 28 5365 (1987)
	JCS Perkin I 699 (1987)
$o\text{-C}_6\text{H}_4(\text{NH}_2)_2$	CL 1117 (1982)
$o\text{-C}_6\text{H}_4(\text{NH}_2)_2$, PhCHO	Syn Commun 15 527 (1985) BCSJ 60 737 (1987)
3,5-dicarboethoxy-2,6-dimethyl-1,4-dihydropyridine, silica	TL 25 3983 (1984) CL 523 (1985) BCSJ 60 2423 (1987)
1-benzyl-1,4-dihydronicotinamide, $\text{Mg}(\text{ClO}_4)_2$	TL 27 2357 (1986)
polymer- 	BCSJ 60 4492 (1987)
baker's yeast (enantioselective)	CL 191 (1987) JOC 54 1802 (1989)

Rhodococcus rhodochrous IFO 3338
(enantioselective)

Agric Biol Chem 49 2331 (1985)

X = PO(OR)₂

H₂, cat Pd-C

J Med Chem 32 1580 (1989); 35 1371 (1992)

H₂, cat [(*t*-Bu)₂PHPdP(*t*-Bu)₂]₂

JOC 59 4027 (1994)

X = SO₂R

H₂, cat [(*t*-Bu)₂PHPdP(*t*-Bu)₂]₂

JOC 59 4027 (1994)

NaBH₄

TL 31 3749 (1990); 32 1267 (1991)

LiHBEt₃

CC 503 (1983)

[HCu(PPh₃)]₆

TL 32 1267 (1991)

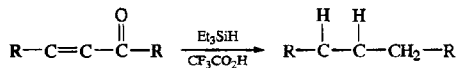


<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
CHO	COR	NaI, HCl	<i>Syn</i> 245 (1980)
COR	COR	SO ₂ , R ₃ N	<i>JOC</i> 59 2599 (1994)
		NaI, HCl	<i>Syn</i> 245 (1980)
		SnCl ₂ , HCl, HOAc	<i>Ber</i> 89 822 (1956)
			<i>JOC</i> 51 4169 (1986)
		TiCl ₃ , H ₂ O	<i>JOC</i> 39 258 (1974)
			<i>Syn</i> 956 (1982)
			<i>JACS</i> 109 7230 (1987)
		Zn, HOAc	<i>JACS</i> 113 3850 (1991)
COR	CO ₂ R	TiCl ₃ , H ₂ O	<i>JOC</i> 39 258 (1974)
CO ₂ H	CO ₂ H	H ₂ , catalyst	M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," Wiley-Interscience, New York (1978), pp 16-18
		H ₂ , cat RuCl ₂	<i>JACS</i> 88 5150 (1966)
		Ti, electrolysis	<i>Can J Chem</i> 56 2269 (1978)
		TiCl ₃ , H ₂ O	<i>JOC</i> 39 258 (1974)
		CrSO ₄	<i>JACS</i> 88 4964 (1966)
		3,5-dicarboethoxy-2,6-dimethyl-1,4-dihydropyridine	<i>JCS</i> 3257 (1960)

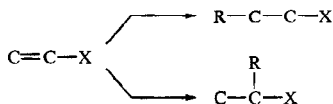
—OCOCO—		3,5-dicarboethoxy-2,6-dimethyl-1,4-dihydropyridine SmI ₂ , HMPA, THF	JCS 3257 (1960) TL 33 5007 (1992)
CO ₂ R	CO ₂ R	SO ₂ , R ₃ N CrSO ₄ LiAlH ₄ , TiCl ₄ , Et ₃ N 3,5-dicarboethoxy-2,6-dimethyl-1,4-dihydropyridine	JOC 59 2599 (1994) JACS 88 4964 (1966) Org Syn 49 98 (1969) TL 28 2393 (1987) JCS 3257 (1960)
CN	CN	CrSO ₄	JACS 88 4964 (1966)
$R_2C=CHXY \longrightarrow R_2CHCHXY$			
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
CO ₂ R	CO ₂ R	NaH / BH ₃ NaBH ₄ LiH ₃ Al(OR)? (R = Me, <i>s</i> -Bu) LiHAl(O- <i>t</i> -Bu) ₃	JACS 113 3085 (1991) JACS 112 834 (1990); 113 3085 (1991) JACS 113 3085 (1991) JACS 113 3085 (1991)
CO ₂ R	CN	HCO ₂ H, Et ₃ N	Chem Pharm Bull 25 2396 (1977)
CN	CN	HCO ₂ H, Et ₃ N	Chem Pharm Bull 25 2396 (1977)
CN	SO ₂ Ph	HCO ₂ H, Et ₃ N	Chem Pharm Bull 25 2396 (1977)



See page 1096, Section 2.15.



TL 36 1387 (1995)



X = COR, CO₂H, CO₂R, CONR₂, CN

See the chapter corresponding to the functional group X.

3.7. Reductive Dimerization



See page 77, Section 1 for intermolecular reactions and page 135, Section 4 for intramolecular reactions.

4. Alkynes



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Parts 3.1–3.3, pp 417–488

4.1. Catalytic Hydrogenation

Reviews:

M. Freifelder, "Practical Catalytic Hydrogenation," Wiley-Interscience, New York (1971), Chpt 8

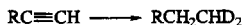
M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley & Sons, New York (1978), Chpt 3

P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 3

Catalysts

$\text{Et}_4\text{N}[\text{HCr}_2(\text{CO})_{10}]$	TL 32 1199 (1991)
Re_2S_7	JACS 76 1519 (1954); 81 3587 (1959)
Ru	IOC 24 708 (1959)
$\text{Rh-Al}_2\text{O}_3$	JACS 111 3640 (1989)
Ni	JCS 5032 (1952)
PtO_2	JACS 74 3636 (1952)

4.2. Hydroalumination-Protonolysis



$i\text{-Bu}_2\text{AlH}/\text{D}_2\text{O}$	Ann 618 267 (1958)
$i\text{-Bu}_2\text{AlH}/\text{Cp}_2\text{TiCl}_2/\text{D}_2\text{O}$	CL 429 (1982)

4.3. Miscellaneous Reagents

Mg, MeOH	TL 30 57 (1988) ($\text{ArC}\equiv\text{CAr}$, $\text{RC}\equiv\text{CCO}_2\text{R}$ only)
NaH, NaO- <i>i</i> -Bu, FeCl_3	TL 3947 (1977)
NaH, NaO- <i>i</i> -Am, $\text{Ni}(\text{OAc})_2$	TL 1069 (1977)

LaNi ₅ H ₆	CC 163 (1984) JOC 52 5695 (1987)
LaNi _{4.5} Al _{0.5} H ₅	JOC 52 5695 (1987)
(EtO) ₃ SiH, cat Pd(OAc) ₂ , cat HC≡CCO ₂ Me, H ₂ O, THF	JOC 55 3452 (1990)
KO ₂ CN=NCO ₂ K, H ⁺	TL 28 5457 (1987)

5. Organic Halides

Reviews:

Syn 425 (1980)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 8, Parts 4.1 (alkyl), 4.5 (vinylic and aryl) and 4.7 (allylic and benzylic)

For reduction of allylic halides with double bond transposition, see page 229, Section 4.



5.1. Low-Valent Metals

Li, NH ₃ (1,1-dichlorobenzocyclobutenes)	Org Prep Proc Int 2 89 (1970)
Li, ROH (3° cyclopropyl)	TL 33 761 (1992)
Li, THF, <i>t</i> -BuOH (alkyl, vinylic, aryl)	Chem Ind 405 (1960) JACS 109 7230 (1987)
Li, THF, <i>t</i> -BuOH, NH ₃ (3° alkyl)	JOC 52 4784 (1987)
Li(Hg), EtOH (dihalocyclopropanes)	JACS 91 1767 (1969)
Na(Hg), MeOH (vinylic)	JOC 56 1192 (1996)
Na, EtOH (dihalocyclopropane; 2°, 3° alkyl; vinylic)	JOC 44 4979 (1979); 56 4020 (1991)
Na, ROH (3° cyclopropyl)	TL 33 761 (1992)
Na, THF, <i>t</i> -BuOH (alkyl, vinylic, aryl)	Org Syn 48 68 (1968) JACS 108 1265 (1986); 114 5018 (1992) JOC 53 5168 (1988); 59 661 (1994)
Na, NH ₃ (cyclopropyl, vinylic)	Org Syn Coll Vol 6 731 (1988) TL 33 6379 (1992)
Na-K, tris(3,6-dioxahexyl)amine (2° alkyl)	TL 28 2503 (1987)
Na-K, dicyclohexyl-18-crown-6 (3° alkyl)	JACS 115 497 (1993)
K, ROH (3° cyclopropyl)	TL 33 761 (1992)
K, crown ether, toluene (alkyl F and Cl)	TL 22 2583 (1981)
Mg/D ₂ O (aryl)	JACS 106 1750 (1984)
Mg, <i>t</i> -PrOH (alkyl, vinylic, aryl)	Proc Chem Soc 219 (1963)

Mg, TiCl ₃ , THF (alkyl, aryl)	CC 781 (1975)
Mg, CdCl ₂ , H ₂ O (benzylic)	TL 34 1681 (1993)
Zn/H ₂ O (R ₂ Cl)	JOC 57 4749 (1992)
Zn, D ₂ O (2° alkyl)	JOC 50 2557 (1985)
Zn, HOAc (alkyl, allylic, aryl)	Org Syn Coll Vol 2 320 (1943) JACS 91 1767 (1969) TL 28 3225 (1987)
Zn, NaOH (aryl)	SL 339 (1990)
Zn, KOH, ROH (cyclopropyl)	JOC 37 1734 (1972)
Zn, KI, CH ₃ OH (RCOCH=CClR)	JACS 72 1645 (1972)
Zn, H ₂ O, cat NiCl ₂ -NaI-PPh ₃ (aryl, 3° alkyl)	JOC 47 2622 (1982)
Zn, H ₂ O, cat NiCl ₂ ·6H ₂ O (2° alkyl)	JOC 56 5125 (1991); 57 4676 (1992); 60 5570 (1995) TL 34 3239 (1993)
Zn-Cu, NH ₄ Cl, EtOH (2° allylic)	JOC 55 1667 (1990)
Zn-Ag, CH ₃ OH (RCOCH=CClR)	JOC 41 636 (1976)
CrCl ₂ , RSH (3° alkyl)	TL 36 2427 (1995)
CrSO ₄ , DMF, H ₂ O (1°, 2° alkyl; allylic; benzylic)	JACS 85 2768 (1963)
Cr(CIO ₄) ₂ (EDA) ₂ , DMF, H ₂ O (alkyl, aryl)	JACS 88 4094 (1966); 92 137 (1970) Angew Int 7 247 (1968) Tetr 24 3503 (1968) Org Syn 52 62 (1972) Org Syn Coll Vol 6 821 (1988)
Cr(CIO ₄) ₂ , EDA, <i>n</i> -BuSH (electrolysis) (1°, 2° alkyl)	Angew Int 19 46 (1980)
SmI ₂ , THF (1° RBr, RI; benzylic chloride, bromide)	JACS 102 2693 (1980) JOC 58 5008 (1993)
Cp ₂ Yb(DME), Mg, CpTi/H ⁺ (aryl)	TL 35 1095 (1994)

5.2. Metal Hydrides

Reviews:

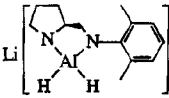
JOC 45 849 (1980)


J. Seyden-Penne, "Reductions by the Alumino- and Borohydrides in Organic Synthesis,"
VCH-Lavoisier (1991), Chpt 1

LiH, <i>t</i> -BuOH, Ni(OAc) ₂ (1°, 3° alkyl; aryl)	TL 36 6051 (1995)
NaH, NaO- <i>t</i> -Am, Ni(OAc) ₂ or ZnCl ₂ (1°, 2°, 3° alkyl; vinylic; allylic; benzylic; aryl)	TL 3951 (1977) JOC 46 1270 (1981)
KH (1° alkyl)	JOC 52 4299 (1987)
KH, cat (<i>i</i> -Bu) ₃ B (1° alkyl)	TL 29 3195 (1988)

MgH ₂ , HMgOC ₆ H ₅ [CH(CH ₃) ₂] ₂ -2,6 (1° RI)	JOC 43 1557 (1978)
NaBH ₄ , DMSO (3° alkyl, allylic, benzylic)	TL 3495 (1965) JACS 88 1473 (1966) JOC 34 3923 (1969); 51 3502 (1986) CC 338 (1970)
NaBH ₄ , DMSO or HMPA or sulfolane (1°, 2° alkyl)	JOC 43 2259 (1978)
NaBH ₄ , sulfolane (3° alkyl)	JOC 36 1568 (1971)
NaBH ₄ (phase transfer) (1°, 2° alkyl; benzylic)	JOC 46 3909 (1981)
NaBH ₄ , KOH, glycols (2° alkyl)	TL 32 2727 (1991)
NaBH ₄ , H ₂ O, CH ₃ CN, hv (aryl)	JACS 95 5085 (1973)
NaBH ₄ , (<i>t</i> -BuO) ₂ , hv (aryl)	TL 27 109 (1986)
NaBH ₄ , cat (Me ₃ Si) ₃ SiH, (ArO) ₂ , hv (1° RBr, RI; 3° RBr; 2° allylic I; ArBr)	TL 30 2733 (1989)
NaBH ₄ , KOH, cat <i>n</i> -Bu ₃ SnH, tetraethylene glycol (2° alkyl)	TL 32 2727 (1991)
NaBH ₄ , (HO) _n Sn(CH ₂ CH ₂ CO ₂ K) ₂ , [HO ₂ CCH ₂ CH ₂ C(CH ₃)(CN)N=] ₂ , KOH (aryl)	TL 35 6221 (1994)
NaBH ₄ , benzo-15-crown-5, polymer-Sn(<i>n</i> -Bu) ₂ Cl (1°, 2° alkyl; aryl)	JOC 54 5138 (1989)
NaBH ₄ , cat R ₃ SnCl (R = Me, <i>n</i> -Bu), hv (1°, 2° alkyl; aryl)	JOC 40 2554 (1975)
NaBH ₄ , Cp ₂ TiCl ₂ (aryl)	JOC 59 940 (1994)
NaBH ₄ , NiCl ₂ , CH ₃ OCH ₂ CH ₂ OH (aryl)	JOC 57 6669 (1992)
NaBH ₄ , cat Ni(II)-tetraazacycles (aryl)	JOC 59 5381 (1994)
NaBH ₄ , cat Ni(PPh ₃) ₄ (aryl)	JOC 44 309 (1979)
NaBH ₄ , NiCl ₂ ·6H ₂ O (1°, 2° alkyl)	Ber 113 3067 (1980) TL 29 4221 (1988); 30 5729 (1989)
NaBH ₄ -anion exchange resin, cat Ni(OAc) ₂ , MeOH (1°, 2°, 3° alkyl; aryl)	Bull Korean Chem Soc 14 543 (1993) JOC 59 4687 (1994)
NaBH ₄ , cat Pd-C (aryl)	Helv 51 2090 (1968)
NaBH ₄ , Et ₃ SiH, cat Pd-C, KOH (ArCl)	TL 34 3263 (1993)
NaBH ₄ , PdCl ₂ (aryl)	TL 4699 (1973) CL 1029 (1981)
NaBH ₄ , cat PdCl ₂ , KOH, CH ₃ OCH ₂ CH ₂ OH, tetraethylene glycol (ArCl)	TL 34 3263 (1993)
NaBH ₄ , Cu ₂ Cl ₂ , MeOH (aryl)	JOC 54 5308 (1989)
Zn(BH ₄) ₂ (3° alkyl, benzylic)	Angew Int 22 562 (1983)

NaBH ₃ CN (1° RCl, RBr, RI; 2° RBr, RI; allylic; benzylic)	Syn 35 (1975) JOC 42 82 (1977); 60 279 (1995) Org Syn Coll Vol 6 376 (1988) JACS 115 2239 (1993)
NaBH ₃ CN-polymer (1° RBr, RI)	JOC 42 82 (1977) CC 1088 (1979)
(<i>n</i> -Bu ₄ N)BH ₃ CN (1° RCl, RBr, RI; 2° RBr, RI; allylic; benzylic)	JOC 42 82 (1977)
NaBH ₃ CN, <i>n</i> -Bu ₃ SnCl (RCCl ₃ → RCH ₂ Cl)	TL 34 5227 (1993)
NaBH ₃ CN, ZnCl ₂ (3° alkyl, allylic, benzylic)	TL 24 3369 (1983)
Na or K[H(CN)B \bigcirc], HMPA (allylic, benzylic)	JOC 42 82 (1977)
LiR ₂ B \bigcirc (3° alkyl, allylic, benzylic)	JACS 97 2558 (1975) Tetr 37 2261 (1981)
LiHBEt ₃ (1°, 2° alkyl; 1°, 2° benzylic)	JACS 95 1669 (1973); 107 2046 (1985) JOC 45 849 (1980); 47 2590 (1982)
LiHBEt ₃ , cat Pd(PPh ₃) ₄ (1° allylic Cl)	JOC 47 4380 (1982)
KHBEt ₃ (1° alkyl)	Bull Korean Chem Soc 8 285 (1987)
KHB(<i>sec</i> -Bu) ₃ (1° alkyl)	Bull Korean Chem Soc 10 382 (1989)
KHB(<i>sec</i> -Bu) ₃ , CuI (1° alkyl, aryl)	CC 762 (1974)
KHBPh ₃ (1° alkyl)	JOC 52 5564 (1987)
NaHB(OMe) ₃ (1° allylic)	TL 28 5977 (1987)
NaH ₂ B(OCH ₂ CH ₂ OCH ₃) ₂ , KOH, tetraethylene glycol (2° alkyl)	TL 32 2727 (1991)
NaH ₂ B(OCH ₂ CH ₂ OCH ₃) ₂ , NiCl ₂ (ArCl)	TL 34 3263 (1993)
LiH ₃ BN \bigcirc (1° alkyl, 1° benzylic)	JOC 59 6378 (1994)
"Pd(PPh ₃) ₂ " / <i>i</i> -Bu ₂ AlH (allylic)	JOC 56 2918 (1991)
LiAlH ₄ (1°, 2°, 3° alkyl; benzylic)	JACS 70 3664, 3738 (1948); 71 1675 (1949); 94 8905 (1972); 114 6227 (1992) TL 2483 (1973); 28 3883 (1987) JOC 45 849 (1980); 47 276 (1982); 49 3545 (1984); 56 1596 (1991)
LiAlH ₄ (aryl)	JOC 33 619 (1968); 34 3918 (1969) TL 1223 (1969)
LiAlH ₄ (vinylic)	TL 36 4223 (1995)
LiAlH ₄ , ultrasound (aryl)	TL 23 1643 (1982)
LiAlH ₄ ·MeN \bigcirc (1° alkyl, 1° benzylic)	TL 35 1515 (1994)

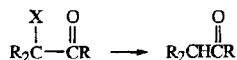
LiAlH_4 , TiCl_3 (aryl)	Rec Trav Chim 101 112 (1982)
LiAlH_4 , TiCl_4 (aryl, vinylic)	CL 291 (1973)
LiAlH_4 , CoCl_2 (2° alkyl)	JACS 108 67 (1986)
LiAlH_4 , CoCl_2 or NiCl_2 (1°, 2°, 3° alkyl; aryl)	TL 4481 (1977) JOC 43 1263 (1978)
$\text{NaH}_2\text{AlEt}_2$ (1° alkyl, 1° benzylic)	Bull Korean Chem Soc 13 199 (1992)
$\text{LiAlH}(\text{i-Bu})_2(\text{n-Bu})$ (1° alkyl, benzylic, allylic)	JOC 49 1717 (1984)
$\text{LiAlH}(\text{OCH}_3)_3$, CuI (1°, 2°, 3° alkyl; aryl; allylic; vinylic)	JACS 95 6452 (1973)
 (1° alkyl, chiral)	TL 33 879 (1992)
Et_3SiH , cat Pd-C (ArCl)	TL 34 3263 (1993)
R_3SiH ($\text{R} = \text{Et}$, n-Bu) or n-BuSiH_3 , cat AlCl_3 (1°, 2°, 3° alkyl)	JOC 41 1393 (1976)
$(\text{Me}_3\text{Si})_3\text{SiH}$ (1°, 2°, 3° alkyl; $\text{R}_2\text{CCl}_2 \longrightarrow \text{R}_2\text{CHCl}$)	JOC 53 3641 (1988); 56 678 (1991) SL 285 (1992) JACS 116 10781 (1994)
$(\text{Me}_3\text{Si})_3\text{SiH}$, Et_3B ($\text{R}_2\text{CCl}_2 \longrightarrow \text{R}_2\text{CHCl}$)	JACS 117 8017 (1995)
$(\text{Me}_3\text{Si})_2\text{SiHMe}$ (1° alkyl, aryl)	JOC 57 3405 (1992)
$(\text{RS})_3\text{SiH}$ (1°, 2°, 3° alkyl)	SL 219 (1990) JOC 57 2427 (1992)
$\text{Me}_3\text{Si}(\text{OSiHMe})_n\text{OSiMe}_3$, cat $\text{Pd}(\text{PPh}_3)_4$, $(\text{PhCH}_2)_3\text{N}$, Δ (aryl)	JOC 51 734 (1986)
R_3SnH ($\text{R} = \text{n-Bu}$, Ph) (alkyl, aryl, vinylic)	JOC 28 703, 2332 (1963); 56 7169 (1991); 57 4457, 4749 (1992); 58 1821, 3877 (1993); 59 1166 (1994) Adv Organometal Chem 1 47 (1964) JACS 87 4007 (1965); 112 3156 (1990); 113 9701 (1991) (α -iodo ester); 116 10781 (1994) (gem dichlorides) Acct Chem Res 1 299 (1968) CC 875 (1969); 882 (1988) (α -chloro ketone) Syn 499 (1970); 665 (1987) ($\text{n-Bu}_3\text{SnH}$ review) TL 28 3883 (1987); 31 2845 (1990) (α -bromo ester); 32 27 (1991) (α -halo ester); 33 6379 (vinylic), 6673 (1992); 35 7861 (1994); 36 7639 (1995) (α -halo ester)
R_3SnH ($\text{R} = \text{n-Bu}$, Ph), ultrasound (1°, 2° alkyl)	JACS 111 6849 (1989) TL 34 1317 (1993) JOC 60 6980 (1995)

$n\text{-Bu}_3\text{SnH}$, Et_3B (2°, 3° alkyl)	TL 34 1317 (1993) JOC 59 1166 (1994); 60 6980 (1995)
$[\text{MeO}(\text{CH}_2)_2\text{O}(\text{CH}_2)_3]_3\text{SnH}$ (1°, 2° alkyl; aryl)	TL 31 2957 (1990)
$(\text{PhCMe}_2)_3\text{SnH}$ (2-halo-3-alkanelactam)	TL 30 3905 (1989)
Ph_3SnH , electrolysis (2-halo-3-alkanelactam)	TL 33 6945 (1992)
$o\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{SnMe}_2\text{H}$ (1° alkyl, allylic, aryl)	JOC 58 3046 (1993)
 $\text{CH}_2\text{CH}_2\text{SnPh}_2\text{H}$ (aryl)	JOC 60 2607 (1995)
polymer- SnR_2H (alkyl, aryl)	JOC 56 5971 (1991) SL 952 (1994)
$\text{HFe}(\text{CO})_4^-$ -polymer (2° benzylic)	JOC 43 1598 (1978)
$\text{LiHCu}(n\text{-Bu})$ (2°, 3° alkyl; aryl)	JACS 96 3686 (1974)
Li_4CuH_5 (1° alkyl)	TL 3695 (1977) JOC 43 183 (1978)

5.3. Miscellaneous Reagents

H_2 , cat Raney Ni (1° alkyl, aryl)	JOC 52 3200 (1987); 54 2103 (1989); 58 4023 (1993)
H_2 , cat Pd-C (2° alkyl, aryl)	JOC 56 4325 (1991); 58 419 (1993)
H_2 , cat Pd-C, KOH, Aliquat 336 (aryl)	JOC 58 5256 (1993); 59 3830 (1994); 60 2430 (1995)
H_2 , cat $\text{Pd}(\text{OH})_2\text{-C}$, Et_3N (aryl)	JOC 60 2292 (1995)
H_2 , cat Pd- CaCO_3 (aryl)	JACS 114 5946 (1992)
H_2 , cat Pd-poly(<i>N</i> -vinyl-2-pyrrolidone) (benzyl, aryl)	TL 35 4599 (1994)
<i>N</i> -benzyl-1,4-dihydronicotinamide; cat $\text{ClRh}(\text{PPh}_3)_3$ or $\text{Pd}(\text{OAc})_2$ (allylic, benzylic, aryl, vinylic)	JOC 50 3283 (1985)
$\text{NaH}_2\text{PO}_2\cdot\text{H}_2\text{O}$, Na_2CO_3 , cat Pd-C, H_2O (benzylic, aryl)	JOC 50 3408 (1985)
$(\text{R}_3\text{NH})\text{H}_2\text{PO}_2$ (3° alkyl)	TL 33 5709 (1992) JOC 58 6838 (1993)
HCO_2H , cat Pd-C, DMF (aryl)	Syn 876 (1982) JOC 57 399 (1992)
NaO_2CH , cat $\text{Pd}(\text{PPh}_3)_4$ (aryl)	TL 1913 (1978) JOC 57 734 (1986)
MO_2CH ($\text{M} = \text{Na}$, NH_4 , Et_3NH), cat Pd-C (aryl)	TL 32 7191 (1991) JOC 60 1347 (1995)
KO_2CH , cat Pd-C (aryl)	JOC 56 6145 (1991)

$(\text{NH}_4)_2\text{O}_2\text{CH}$, cat Pd-C (aryl)	JOC 54 1284 (1989)
$(\text{Et}_3\text{NH})\text{O}_2\text{CH}$, cat Pd-C or $(\text{Ar}_3\text{P})_2\text{Pd}(\text{OAc})_2$ (aryl)	JOC 42 3491 (1977)
NaOCH_3 , cat $\text{Pd}(\text{PPh}_3)_4$ (aryl)	JOC 43 1619 (1978)
$n\text{-BuLi}/\text{H}_2\text{O}$ (halocyclopropane)	JACS 112 3156 (1988)
$t\text{-BuLi}/\text{H}_2\text{O}$ (1° alkyl)	JOC 55 5404 (1990)
EtMgBr , cat $\text{PdCl}_2(\text{dppf})$ (1° alkyl)	TL 30 4779 (1989) JOC 55 6188 (1990)
Et_2Zn , cat $\text{Pd}(\text{PPh}_3)_4$ (benzylic)	JOC 58 6908 (1993)
KPPH_2 (1,1-dichlorocyclopropanes to chlorocyclopropanes)	JOC 52 3923 (1987)
$\text{KP}(\text{O})(\text{OMe})_2$ (1,1-dibromocyclopropanes to bromocyclopropanes)	JOC 50 3713 (1985)
$(\text{MeO})_2\text{P}(\text{O})\text{H}$, cat $(\text{PhCO}_2)_2$ (2° , 3° alkyl)	TL 33 2311 (1992) JOC 58 6838 (1993)
$(\text{EtO})_2\text{P}(\text{O})\text{H}$, Zn, VCl_3 (dibromocyclopropanes to bromocyclopropanes)	JOC 58 6529 (1993)
AlCl_3 , EtSH (polycyclic aryl)	TL 23 689 (1982)
$h\nu$, Et_3N (2° alkyl)	TL 35 8161 (1994)
$h\nu$, Et_3N , anthracene (aryl)	CC 1703 (1987)
$h\nu$, THF [α -(iodoalkylidene)lactones]	TL 30 5159 (1989)
$h\nu$, MeOH or hexane (R_fX)	JOC 59 1115 (1994)
electrolysis (dihalo to monohalocyclopropanes, 1° alkyl, aryl)	JACS 91 1767 (1969) JOC 55 1065, 3897 (1990) TL 33 1499 (1992)




Reviews:

Org Rxns 29 163 (1983)

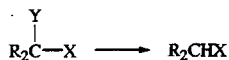
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 4.8, p 983

H_2 , cat Pd-C ($\text{X} = \text{Br}$)	JOC 23 1938 (1958)
HClO_4 , 10-methylacridan ($\text{X} = \text{Cl}, \text{Br}$)	JACS 111 1497 (1989)
HClO_4 , 1,1'-dimethylferrocene ($\text{X} = \text{Cl}, \text{Br}$)	JACS 111 1497 (1989)
HI ($\text{X} = \text{Br}, \text{I}$)	JCS 4356 (1956) JACS 81 3634 (1959)

HI or NaI, H ₃ PO ₂ (X = Cl, Br)	SL 554 (1990)
LiI, BF ₃ (X = Cl, Br, I)	TL 137 (1971)
NaI, R ₃ N (R = Me, Et), SO ₂ (X = Cl, Br)	Syn 59 (1979)
NaI, py, SO ₃ (X = Cl, Br)	Syn 59 (1979)
NaI, HOAc (X = Br)	JOC 16 573 (1951)
NaI, aq H ₂ SO ₄ (X = Cl, Br, I)	TL 21 3195 (1980)
NaI, Me ₃ SiCl (X = Cl, Br)	JOC 45 3531 (1980)
NaI, MeSiCl ₃ (X = Br)	JOC 48 3667 (1983)
NaI, SnCl ₂ , H ₂ O, THF (X = Cl, Br)	Syn 570 (1986)
Me ₃ SiI (X = Cl, Br)	Syn Commun 11 101 (1981)
PI ₃ or P ₂ I ₄ (X = Br, I)	TL 22 1431 (1981)
Fe graphite (X = Br)	JOC 47 876 (1982)
Zn, H ₂ O, DMSO, C ₆ H ₆ (X = Cl)	JOC 52 5280 (1987)
Zn, H ⁺ (X = Br)	JACS 81 3127, 3634, 3644 (1959) JOC 36 1153 (1971)
Zn, HOAc (X = Cl, Br)	Ann 681 196 (1965) JOC 37 2363 (1972); 45 2036 (1980); 48 2590 (1983); 50 3957 (1985); 52 4772 (1987); 53 3803 (1988) JACS 101 4003 (1979); 105 2435 (1983)
Zn, HOAc, EtOH, TMEDA (X = Cl)	TL 28 3299 (1987) (4,4-dichlorocyclobutenones to cyclobutenone)
Zn, HOAc, KI (X = Cl)	JACS 83 3114 (1961)
Zn-Cu, NH ₄ Cl, ROH (X = Cl, I)	JACS 110 8591 (1988) TL 29 159 (1988) JOC 59 1389 (1994)
SnCl ₂ , HCl (X = Br)	JACS 68 1813 (1946)
SnCl ₂ , <i>i</i> -Bu ₃ AlH (X = Br)	CL 2069 (1984)
TiCl ₃ (X = Cl, Br)	Syn Commun 3 237 (1973) JACS 108 1239 (1986) TL 28 1541 (1987)
Ti ₂ (SO ₄) ₃ (X = Cl, Br)	TL 28 1541 (1987)
VCl ₂ (X = Cl, Br)	Syn 807 (1976)
CrSO ₄ , H ₂ O, DMF (X = Cl, Br)	JACS 85 2768 (1963)
CrCl ₂ (X = Br, I)	JACS 67 1728 (1945); 72 4077 (1950) JCS 3869 (1953)

CrCl_3 , LiAlH_4 ($X = \text{Br}$)	TL 3829 (1977)
$\text{Ce}_2(\text{SO}_4)_3$, NaI ($X = \text{Cl}, \text{Br}$)	Syn Commun 9 241 (1979)
SmI_2 , MeOH ($X = \text{Cl}$)	JOC 51 1135 (1986)
NaBH_4 , NiCl_2 ($X = \text{Cl}, \text{Br}$)	TL 26 4657 (1985)
NaBH_4 , $\text{Ni}(\text{OAc})_2$ or $\text{Pd}(\text{OAc})_2$ or $\text{Pd}(\text{NO}_3)_2$ or $\text{Hg}(\text{OAc})_2$ ($X = \text{Br}$)	TL 513 (1961)
PhSiH_3 , cat $\text{Mo}(\text{CO})_6$, (cat PPh_3), NaHCO_3 ($X = \text{Cl}, \text{Br}$)	JOC 52 5570 (1987)
Ph_2SiH_2 , cat $\text{Pd}(\text{PPh}_3)_4$ ($X = \text{Br}$)	JOC 52 5570 (1987)
$\text{Me}_3\text{Si}(\text{OSiHMe})_n\text{OSiMe}_3$ or NaO_2CH , cat $\text{Pd}(\text{PPh}_3)_4$ ($X = \text{Br}$)	JOC 51 734 (1986)
$(\text{RS})_3\text{SiH}$ ($X = \text{Cl}, \text{Br}$)	JOC 57 2427 (1992)
$(\text{Me}_3\text{Si})_2\text{SiHMe}$ ($X = \text{Cl}, \text{Br}$)	JOC 57 3405 (1992)
R_3SnH or R_2SnH_2 ($\text{R} = n\text{-Bu}, \text{Ph}$) ($X = \text{Cl}, \text{Br}$)	JOC 28 2165 (1963) TL 31 6381 (1990)
$n\text{-Bu}_3\text{SnH}$ ($X = \text{Cl}$)	JOC 52 307 (1987)
Ph_3SnH ($X = \text{Cl}, \text{Br}$)	JOC 51 5182 (1986)
$(\text{PhMe}_2\text{CCH}_2)_3\text{SnD}$ ($X = \text{Br}$)	JOC 59 3747 (1994)
$\alpha\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{SnMe}_2\text{H}$ ($X = \text{Br}$)	JOC 58 3046 (1993)
polymer- SnR_2H ($X = \text{Br}$)	JOC 56 5971 (1991)
$\text{HFe}(\text{CO})_4^-$ -polymer ($X = \text{Br}$)	JOC 43 1598 (1978)
$(\text{Et}_4\text{N})\text{HFe}_3(\text{CO})_{11}$ ($X = \text{Br}$)	JOMC 171 85 (1979)
$\text{Fe}(\text{CO})_5$ ($X = \text{Br}$)	JOC 44 641 (1979)
$\text{Fe}(\text{CO})_5$, KOH ($X = \text{Br}$)	TL 2257 (1975)
$\text{Fe}_2(\text{CO})_9$, H_2O , DMF ($X = \text{Br}$)	IACS 94 7202 (1972); 100 1759 (1978)
$\text{Mo}(\text{CO})_6$, Al_2O_3 ($X = \text{Br}$)	JOC 44 2568 (1979)
cat $\text{Co}_2(\text{CO})_8$, NaOH , $(\text{PhCH}_2\text{NEt}_3)\text{Cl}$ ($X = \text{Br}$)	TL 2861 (1977)
PhNMe_2 ($X = \text{Br}$)	Chimia 21 464 (1967)
$\text{ArCH}_2\text{NH}_2 / \text{KO-}t\text{-Bu} / \text{H}_3\text{O}^+$ ($X = \text{Cl}, \text{Br}$)	JOC 57 5761 (1992)
DMBI ($X = \text{F}, \text{Cl}, \text{Br}$)	JOC 51 5400 (1986) (α -halo aldehydes, ketones); 54 3842 (1989)
DMBI , PhSH ($X = \text{Cl}, \text{Br}$)	JOC 57 662 (1992)
RNHCO  ($X = \text{F}, \text{Cl}, \text{Br}$)	JOC 52 2142 (1987)
N -benzyl-1,4-dihydronicotinamide; cat $\text{ClRh}(\text{PPh}_3)_3$ or $\text{Pd}(\text{OAc})_2$ ($X = \text{Cl}, \text{Br}$)	JOC 50 3283 (1985)

Ph ₂ PH (X = Cl, Br)	JOC 34 2687 (1969)
Ph ₃ P, MeOH, C ₆ H ₆ (X = Cl, Br)	TL 471, 583 (1962) IACS 85 2183 (1963) JCS 1379 (1965) JOC 31 4031 (1966)
PhSH, iron polyphthalocyanine (X = Cl, Br)	CL 1241 (1975)
RS ⁻ (X = Cl, Br, I)	BCSJ 44 828 (1971) JOC 46 2596 (1981)
NaHSO ₃ (X = I)	IACS 72 362 (1950)
Na ₂ S ₂ O ₄ , H ₂ O, DMF (X = Cl, Br)	Syn Commun 12 261 (1982)
py / Na ₂ S ₂ O ₄ (X = Cl, Br)	JOC 39 562 (1974)
PhSeH, K ₂ CO ₃ (X = I)	JOC 46 2596 (1981)
NaTeH (X = Cl, Br)	CL 119 (1983)
(Ph ₃ Sn) ₂ Te, KF·2H ₂ O (X = Cl, Br)	TL 32 1545 (1991)
ThTeLi(Na) (X = Cl, Br, I)	JOC 47 3946 (1982)
(EtO) ₂ P(O)TeNa (X = Cl, Br)	JOC 47 1124 (1982)



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
CO ₂ H	Cl	Zn, HOAc	TL 28 5339 (1987)
		ThTeLi(Na)	JOC 47 3946 (1982)
	Br	DMBI	JOC 51 5400 (1986)
		HI or NaI, H ₃ PO ₃	SL 554 (1990)
CO ₂ R	Cl	H ₂ , cat Pd-C	JOC 52 3777 (1987)
		Al(Hg), H ₂ O, THF	JOC 58 3172 (1993)
		Zn, HOAc	TL 28 5339 (1987)
		Zn-Cu, H ₂ O	SL 962 (1992)
		NaH ₂ PO ₄ ·H ₂ O, Na ₂ CO ₃ , cat	JOC 50 3408 (1985) (2,2-dihalo-
		Pd-C, H ₂ O	alkanoate ester to 2-halo-
	Cl, Br		alkanoate ester)
		NaI, SnCl ₂ , H ₂ O, THF	Syn 570 (1986)
		NaTeH	CL 119 (1983)
		NaBH ₄ -anion exchange resin,	JOC 59 4687 (1994)
		cat Ni(OAc) ₂ ·4H ₂ O, MeOH	
		PhSiH ₃ , cat Mo(CO) ₆ , cat	JOC 52 5570 (1987)
	Br	PPh ₃ , NaHCO ₃	
		n-Bu ₃ SnH	JOC 58 3877 (1993)
		DMBI	JOC 51 5400 (1986)
		HI or NaI, H ₃ PO ₃	SL 554 (1990)
		n-Bu ₃ SnH	TL 31 2845 (1990); 32 2857 (1991)
		HOCH ₂ CH ₂ SH, 1,2,2,6,6-pentamethylpiperidine, cat	TL 36 3997 (1995)
		t-BuONNO-t-Bu	

		SmI ₂ , CH ₃ OH	JOC 51 1135 (1986)
		HFe(CO) ₄ ⁻ -polymer	JOC 43 1598 (1978)
	I	<i>n</i> -Bu ₃ SnH	JOC 60 288 (1995)
CONR ₂	Cl	Zn, HOAc	TL 28 5339 (1987)
		NaH ₂ PO ₄ ·H ₂ O, Na ₂ CO ₃ , cat	JOC 50 3408 (1985) (2,2-dihalo-
		Pd-C, H ₂ O	alkanamide to 2-haloalkan-
			amide)
	Br	(PhMe ₂ CCH ₂) ₃ SnD	JOC 59 3747 (1994)
		NaTeH	CL 119 (1983)
		ThTeLi(Na)	JOC 47 3946 (1982)
	Br, I	H ₂ , cat CIRh(PPh ₃) ₃	JOC 54 2233 (1989)
		H ₂ , cat Rh-Al ₂ O ₃	JOC 54 2235 (1989)
		H ₂ , cat Pd-CaCO ₃	JOC 54 2235 (1989)
CN	Br	HI or NaI, H ₃ PO ₃	SL 554 (1990)



X = halogen

H₂, cat Pd-C

Can J Chem 37 1870 (1959)

JACS 104 2198 (1982); 109 4752 (1987)

Li, NH₃, EtOH

TL 28 3209 (1987)



X = Br, I

JACS 110 5567 (1988)

TL 34 1155 (1993)

6. Amines and Derivatives



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 4.2, p 811

RSO₂Cl (R = Ph, *p*-Tol, Me)/H₂NOSO₃H, NaOH JACS 82 753 (1960); 86 1152 (1964)

RSO₂Cl (R = CF₃, *p*-Tol, *p*-BrC₆H₄, *p*-NO₂C₆H₄) JOC 40 2018 (1975); 43 2259 (1978)
(disulfonimide)/NaBH₄, HMPA

H₂NOSO₃H, OH⁻ JACS 100 341 (1978)

MeCO₂CHO/POCl₃/*n*-Bu₃SnH, AIBN JACS 90 4182 (1968)
TL 2291 (1979)
CC 345 (1979)
Syn 68 (1980)

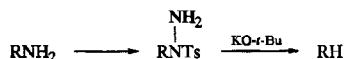
2,4,6-triphenylpyrylium perchlorate/NaBH₄/Δ TL 2689 (1976)

HNF₂ JACS 85 97 (1963); 86 2233 (1964)

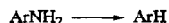
$\text{NaNO}_2, \text{H}_3\text{PO}_2, \text{cat Cu}_2\text{O}$ (R = aryl)	JACS 108 1000 (1986)
<i>i</i> -AmONO, H_2SO_4 , hydroquinone, dioxane (R = aryl)	CC 605 (1973)
<i>n</i> -AmONO, THF (R = aryl)	JCS Perkin I 541 (1973)
RONO (R = <i>t</i> -Bu, PhCH_2), DMF (R = aryl)	JOC 42 3494 (1977)
HNO_3 , electrolysis (R = aryl)	SL 439 (1995)



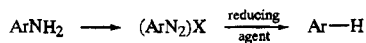
JOC 57 3772 (1992)



TL 33 7465 (1992)



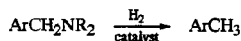
<i>t</i> -BuONO, DMF	JOC 42 3494 (1977); 59 5535 (1994)
<i>n</i> -AmONO, THF	JCS Perkin I 541 (1973)



Review: Org Rxs 2 262 (1944)

H_3PO_2	JACS 71 2137 (1949); 72 3013 (1950); 76 290 (1954) Org Syn Coll Vol 3 295 (1955); 4 947 (1963)
H_3PO_3	JACS 71 2137 (1949); 72 3013 (1950); 74 3074 (1952)
$\text{Ca}(\text{H}_2\text{PO}_2)_2$	Ber 35 162 (1902)
NaBH_4 , DMF	JACS 83 1251 (1961)
Et_3SiH or <i>n</i> - Bu_3SnH	Tetr 26 4609 (1970)
SnCl_2 , NaOH	JACS 64 376 (1942)
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, DMF	JOC 60 1713 (1995)
cat $\text{ClRh}(\text{PPh}_3)_3$ or $\text{ClRh}(\text{CO})(\text{PPh}_3)_2$, DMF	JOC 36 1725 (1971)
cat Cu_2O , dioxane	JOC 32 3844 (1967)
NaOCH_3 , CH_3OH	JOC 33 1924 (1968) CC 1469 (1971)
$\text{KO-}t\text{-Bu}$, <i>t</i> - BuOH , Et_2O	JOC 33 1924 (1968)
PhSH	CL 1051 (1979)
H_2CO	JACS 61 2418 (1939)
HMPA	JOC 39 1317 (1974)
HCONH_2 , Et_3N	JCS Perkin I 873 (1986)

DMF	Ind J Chem B 20 767 (1981)
Me ₂ NCONMe ₂	JOC 28 568 (1963)
	Ind J Chem B 20 767 (1981)
various ethers and 3° amines	Angew 70 211 (1958)



Review: Org Rxs 7 263 (1953)

7. Nitro Compounds

See page 229, Section 4 for reduction with double bond transposition.



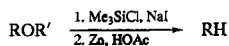
Reviews:

Syn 833 (1988)

N. Ono, "Nitro Compounds: Recent Advances in Synthesis and Chemistry," Eds. H. Feuer and A. T. Nielsen, VCH, New York (1990), Chpt 1

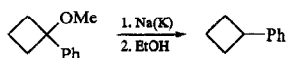
Reagent(s)	R	
Et ₃ SiH, AlCl ₃ or SnCl ₄	benzylic, α- or β-thiophenyl alkyl	TL 28 2277 (1987)
Et ₃ SiH, Na ₂ S ₂ O ₄ , H ₂ O, HMPA	α-ketoalkyl	TL 30 4819 (1989)
n-Bu ₃ SnH, AIBN	2°, 3° alkyl; 2° α-keto-alkyl; 1° allylic or benzylic	JACS 103 1557 (1981) TL 22 1705 (1981); 23 2957 (1982) CC 33 (1982) JOC 50 3692 (1985); 51 2832 (1986); 52 5061 (1987); 54 5453 (1989); 55 5188 (1990) Tetr 41 4013 (1985) Syn 693 (1986) (review) Chem Pharm Bull 36 3714, 3718 (1988)
n-Bu ₃ SnH, NCCr ₂ N=NCR ₂ CN	1° alkyl	TL 36 2595 (1995)
NaTeH, EtOH	3° alkyl	BCSJ 58 1067 (1985)
NaSMe, DMF or HMPA	3° alkyl	JACS 100 289 (1978); 101 647 (1979)
(NH ₄) ₂ O ₂ CH, PPh ₃ , cat Pd(PPh ₃) ₄	allylic	JOC 51 3734 (1986)
KOH, HOCH ₂ CH ₂ OH	2°, 3° alkyl	TL 3203 (1971); 1243 (1979)
1-benzyl-1,4-dihydronicotinamide, hv	α-cyano, -keto or -ester	JACS 102 2851 (1980); 105 4017 (1983)

8. Ethers

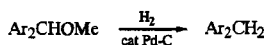


R' = Me, SiMe₃; R = 1°, 2° alkyl or benzylic

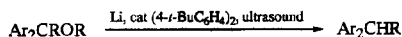
Syn 32 (1981)



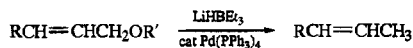
JOC 53 3298 (1988)



JOC 59 4501 (1994)

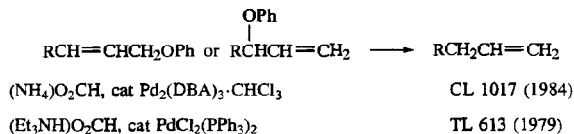


TL 31 6155 (1990)



R' = Me, Ph, SiMe₂(*t*-Bu)

JOC 47 4380 (1982)



X

Reagents

OMe

Na-K/EtOH

JACS 110 900 (1988)

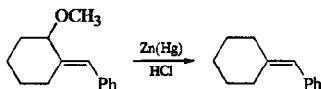
OSiMe₃

Li, NH₃/NH₄Cl

JOC 58 328 (1993)

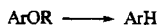
Li, sonication/NH₄Cl

JOC 59 5093 (1994)



TL 725 (1972)

Org Syn Coll Vol 6 725 (1972)



Na, ROH

Ber 69 1643 (1936)

Can J Chem 52 2136 (1974)

K, THF

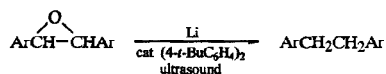
CC 1549 (1987)

EtSH, AlCl₃

TL 23 689 (1982)



TL 31 2589 (1990)



TL 30 4931 (1989)

Reagent(s)R'

Na, anthracene

R

JOC 54 2505 (1989)

Al(Hg), H₂O

R

JACS 110 4726 (1988)

JOC 56 3352 (1991)

HI

1° alkyl

JOC 56 334 (1991)

Me₃SiI, (MeOH)

1° alkyl

JOC 56 334 (1991)

Me₃SiCl, NaI, MeOH

Me

JOC 56 334 (1991)

NaTeH

Me

JACS 110 3670 (1988)

SmI₂

R

JOC 53 5885 (1988)

SL 269 (1992)

TL 34 4369 (1993)

JACS 116 2667, 11287 (1994)

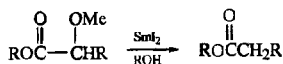
SmI₂, ROHMe, R, SiMe₃, Ts

JOC 51 1135 (1986); 60 3787 (1995)

TL 28 3065 (1987); 29 439

(1988); 35 1477 (1994)

JACS 112 9388 (1990); 116 2153 (1994)



TL 30 2945 (1989); 33 573 (1992)

9. Alcohols and Phenols

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 4.2, p 811

For reduction of allylic alcohols with double bond transposition, see page 229, Section 4.

9.1. Direct Reduction



H ₂ , cat CoCl ₂ , cat KCl, KCN, KOH, β-cyclodextrin	TL 31 4101 (1990) (1°, 2° allylic)
H ₂ , cat Pd-C	JACS 89 4233 (1967) (3° benzylic) JOC 55 3767 (1990); 59 2687 (1994) (both 2° benzylic)
H ₂ , cat Pd-C, KOH, <i>o</i> -C ₆ H ₄ Cl ₂	JOC 60 2430 (1995) (1°, 2°, 3° benzylic)
H ₂ , cat Pt	JACS 89 4233 (1967) (3° benzylic)
H ₂ , cat PtO ₂ , CF ₃ CO ₂ H	JOC 29 2325 (1964) (3° alkyl)
HCO ₂ H	JOC 58 3748 (1993) (Ar ₃ COH)
HCO ₂ H, CF ₃ SO ₃ H	JOC 53 5143 (1988) (3° benzylic)
Li, NH ₃ , NH ₄ Cl	JOC 40 3151 (1975) (1°, 2°, 3° benzylic)
Li, cat (4- <i>t</i> -BuC ₆ H ₄) ₂ , ultrasound	TL 31 6155 (1990) (2°, 3° benzylic)
K, Fe(CO) ₅ / HCl	TL 21 801 (1980) (2°, 3° benzylic)
Raney Ni, EtOH	JACS 89 4233 (1967) (3° benzylic) TL 35 5611 (1994) (3° benzylic)
Raney Ni, toluene	JOC 53 432, 3158 (1988) (both 3° alkyl)
Zn(Hg), HCl	TL 725 (1972) (1°, 2° allylic) Org Syn Coll Vol 6 769 (1988) (2° allylic)
BH ₃ ·py, CF ₃ CO ₂ H	Chem Pharm Bull 27 2405 (1979) (2° benzylic)
BH ₃ , BF ₃ ·OEt ₂	TL 1849 (1967) (3° benzylic cyclopropyl)
NaBH ₄ , HOAc, CF ₃ CO ₂ H	JOC 58 4132 (1993) (2° benzylic)
NaBH ₄ , CF ₃ CO ₂ H	Syn 172 (1977) (2°, 3° benzylic) JOC 53 5143 (1988) (3° benzylic)
NaBH ₄ , CF ₃ SO ₃ H	JOC 53 5143 (1988) (3° benzylic)
NaBH ₄ , BF ₃ ·OEt ₂	Proc Chem Soc 357 (1962) (2° benzylic) J Sci Ind Res B 21 583 (1962) (2° benzylic)
NaBH ₄ , PdCl ₂	CL 1029 (1981) (2° benzylic)
Ph ₃ PO, Tf ₂ O / NaBH ₄	JOC 58 6913 (1993) (1°, 2° alkyl)

NaBH ₃ CN, BF ₃ ·OEt ₂	SL 93 (1995) (1° benzylic) TL 36 2347 (1995) (1° allylic)
NaBH ₃ CN, ZnI ₂	JOC 51 3038 (1986) (1°, 2° benzylic; 2° allylic; 3° alkyl) TL 36 3299 (1995) (3° benzylic)
BR ₃ (R = Et, <i>i</i> -Pr), CF ₃ SO ₃ H <i>i</i> -Bu ₃ Al/AlBr ₃ , cat Cp ₂ TiCl ₂	JOC 56 2759 (1991) (2°, 3° alkyl; 1°, 2°, 3° benzylic) JOC 57 2143 (1992) (2° benzylic)
LiAlH ₄	TL 31 553 (1990) (1°, 2°, 3° benzylic)
LiAlH ₄ , AlCl ₃	JOC 29 121 (1964) (3° alkyl, 3° benzylic) TL 2447 (1967) (2° allylic)
AlCl ₃ , cat Pd-C, cyclohexene	Syn 397 (1978) (1°, 2°, 3° benzylic)
AlCl ₃ , EtSH	TL 23 689 (1982) (polycyclic ArOH)
Et ₃ SiH, LiClO ₄	TL 35 61 (1994) (2° allylic)
R ₃ SiH, BF ₃	TL 2955 (1976) (2° alkyl, 3° benzylic)
Et ₃ SiH, BF ₃ ·OEt ₂	TL 29 5793 (1988) (2° benzylic) IACS 113 5402 (1991) (3° benzylic) JOC 60 5316 (1995) (3° allylic, 3° benzylic, 3° propargylic)
R ₃ SiH (R = Ph, Et), HOAc	IACS 90 2578 (1968) (1°, 2°, 3° benzylic)
Et ₃ SiH, CF ₃ CO ₂ H	JOC 34 4 (1969) (3° benzylic); 36 758 (1971) (3° alkyl); 52 2226 (1987) (2° benzylic); 53 4786 (1988) (2° benzylic) JACS 91 2967 (1969) (3° alkyl; 2°, 3° benzylic; cyclopropyl carbonyl) J Gen Chem USSR 43 2294 (1973) (2° ferrocenyl carbonyl) Syn 633 (1974) (review)
Et ₃ SiH, CF ₃ CO ₂ H, NH ₄ F	SL 647 (1992) (3° alkyl; 2°, 3° benzylic)
Me ₃ SiCl, NaI, CH ₃ CN	TL 28 3817 (1987) (2°, 3° benzylic); 30 4741 (1989) (2°, 3° benzylic)
Me ₃ SiCl, NaI/Zn, HOAc	Syn 32 (1981) (1°, 2° alkyl; 1°, 2° benzylic)
Me ₂ SiI ₂	TL 4941 (1979) (2°, 3° benzylic)
H ₂ S, CO, cat Co ₂ (CO) ₈	JOC 53 3306 (1988) (1° benzylic)
P, I ₂ , HOAc	JOC 23 1139 (1958); 59 7701 (1994) (both Ar ₂ CHOH)
P ₂ I ₄	CL 247 (1983) (1°, 2°, 3° benzylic)
PPh ₃ , I ₂	Ber 109 1586 (1976) (1° allylic, 2° benzylic) TL 35 5261 (1994) (2° benzylic)
R ₃ P, Et ₄ NBr, electrolysis	TL 35 4129 (1994) (1°, 2° alkyl)
WCl ₂ (PMePh ₂) ₄	JACS 112 6413 (1990) (1° alkyl; 1°, 2° allylic)

HI, HOAc, H₂O

JACS 109 4690 (1987)

Li, NH₃

TL 31 3941 (1990)

Zn, HOAc

JCS 3045 (1954)

SmI₂

JACS 110 6558 (1988); 116 9912 (1994)

TL 35 1665 (1994); 36 1661 (1995)

SmI₂, Ac₂O

JOC 51 1135 (1986)

JACS 109 4424 (1987)

Me₃SiI/Na₂S₂O₃, H₂O

Syn Commun 9 665 (1979)

P, I₂

Syn 161 (1975)

Ph₂PLi/HOAc, MeI

JOC 51 2378 (1986)

SmI₂, H₂O, THF

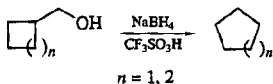
SL 861 (1994) (lactone)

SmI₂, HOCH₂CH₂OH, (HMPA)

TL 33 573 (1992)

SmI₂, Me₃CCO₂H

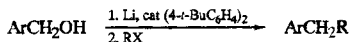
TL 30 2945 (1989)



JOC 54 1452 (1989)

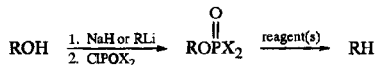


JOC 53 3158 (1988)



TL 31 6155 (1990)

9.2. Via Phosphorus Compounds

XReagent(s)

OEt

electrolysis

Li, NH₃, Et₂OLi or Na, NH₃

JOC 44 4508 (1979) (phenol)

JOC 42 344 (1977) (phenol)

JCS 522 (1955) (phenol)

	Li, Na or K; NH ₃ ; Et ₂ O	JOC 38 2314 (1973) (phenol)
	Ti, THF	JOC 43 4797 (1978) (phenol)
NMe ₂	Li, NH ₃	JOC 45 1172 (1980) (2° alcohol)
	Li, NH ₃ , EtOH, THF	JACS 94 5098 (1972) (2° alcohol)
	Li, MeNH ₂	CC 1342 (1987) (1° alcohol)
	Li, MeNH ₂ , <i>t</i> -BuOH	JOC 57 1968 (1992) (2° alcohol)
	Li, EtNH ₂	JACS 94 5098 (1972) (2° alcohol)
	Li, EtNH ₂ , <i>t</i> -BuOH, THF	JACS 94 5098 (1972) (1°, 2°, 3° alcohol); 108 3835 (1986) (3° alcohol); 111 6257 (1989) (2° alcohol)
		TL 28 2863 (1987) (1° alcohol)

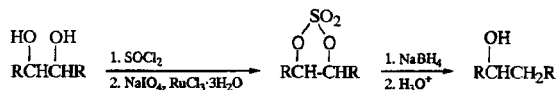
9.3. Via Sulfonates



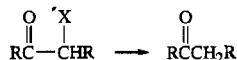
Review: J. Seyden-Penne, "Reductions by the Alumino- and Borohydrides in Organic Synthesis," VCH-Lavoisier (1991), Chpt 1

MsCl/electrolysis (1°, 2° alkyl)	TL 2157 (1979)
MsCl/Li, NH ₃ (2° alkyl)	JACS 111 8231 (1989)
Me ₂ NSO ₂ Cl/Na, NH ₃ (2° alkyl)	TL 3365 (1978)
TsCl or MsCl/NaI, Zn (1°, 2° alkyl)	TL 3325 (1976) Coll Czech Chem Commun 44 246 (1979) JACS 107 2471 (1985)
TsCl/H ₂ , cat Pd-C (2° benzylic)	JOC 59 3821 (1994)
MsCl/KO- <i>t</i> -Bu/H ₂ , cat Pd-C (2° alkyl)	JOC 47 2685 (1982)
MsCl/NaBH ₄ , <i>t</i> -BuOH, CH ₃ OCH ₂ CH ₂ OCH ₃ (1° alkyl)	JOC 52 1309 (1987)
TsCl/NaBH ₄ , DMSO or HMPA or sulfolane (1°, 2° alkyl)	JOC 43 2259 (1978)
TsCl/NaBH ₃ CN (1° alkyl, benzylic)	Syn 135 (1975) JOC 42 82 (1977) Org Syn Coll Vol 6 376 (1988)
TsCl/(<i>n</i> -Bu ₄ N)BIH ₃ CN (1° alkyl)	JOC 42 82 (1977)
TsCl/LiHBEt ₃ (1°, 2° alkyl)	JOC 41 3064 (1976); 45 1 (1980); 50 2668, 5646 (1985); 58 6857 (1993) JOMC 156 171 (1978) Carbohydr Res 110 19 (1982) JACS 108 468 (1986); 109 6858, 8102 (1987) CC 1786 (1987)
MsCl/LiHBEt ₃ (1°, 2° alkyl)	JOC 42 2166 (1977) CC 1139 (1987) JACS 109 6858 (1987); 111 6717 (1989) TL 28 5161 (1987)

$C_5H_5N \cdot SO_3 / LiAlH_4$ (allylic, benzylic)	JOC 34 3667 (1969) TL 1837 (1969); 27 4813 (1986) JACS 92 6636, 6637 (1970)
TsCl or MsCl/LiAlH ₄ (1°, 2° alkyl)	JACS 73 2872 (1951); 77 1820 (1955); 92 553 (1970); 107 686 (1985) JOC 47 2685 (1982); 52 4776 (1987); 53 1982 (1988) TL 30 5729 (1989)
TsCl/LiAlH ₄ , LiH (1° alkyl)	JACS 108 468 (1986)
MsCl/2 LiAl(OMe) ₃ , CuI (1°, 2° alkyl)	JACS 95 6452 (1973)
TsCl/ <i>n</i> -Bu ₃ SnH (2° alkyl)	TL 35 2587 (1994)
TsCl or MsCl/LiHCu(<i>n</i> -Bu) (1°, 2° alkyl; allylic)	JACS 96 3686 (1974)
TsCl/Li ₄ CuH ₅ (1° alkyl)	JOC 43 183 (1978)
TsCl or MsCl/ <i>n</i> -BuZnCl, cat Pd(DBA) ₂ , cat PPh ₃ (3° allylic)	TL 33 3307 (1992)
RSO ₂ Cl (R = Me, CF ₃ , Ar)/(Et ₃ NH)O ₂ CH, cat Pd(OAc) ₂ , cat phosphine or diphosphine (aryl)	JOC 55 350 (1990)
(R _f SO ₂) ₂ /cat PdCl ₂ (PPh ₃) ₂ or Pd(PPh ₃) ₄ , <i>n</i> -Bu ₃ N, HCO ₂ H (aryl)	CC 1452 (1986)
Tf ₂ O/cat PdCl ₂ (PPh ₃) ₂ , cat dppp, <i>n</i> -Bu ₃ N (aryl)	JOC 55 991 (1990)
Tf ₂ O/cat PdCl ₂ (PPh ₃) ₂ , cat dppp, <i>n</i> -Bu ₃ N, HCO ₂ H or HOAc (aryl)	JOC 55 991 (1990)
Tf ₂ O/cat PdCl ₂ (PPh ₃) ₂ , cat dppp, Et ₃ N, HCO ₂ H (aryl)	JOC 57 1262 (1992)
Tf ₂ O/HCO ₂ H, <i>n</i> -Bu ₃ N, cat Pd(OAc) ₂ (PPh ₃) ₂ (aryl)	JACS 110 7419 (1988)
Tf ₂ O/HCO ₂ H, Et ₃ N, PPh ₃ , cat Pd(OAc) ₂ (aryl)	TL 27 5541 (1986); 28 1381 (1987)
Tf ₂ O/H ₂ , cat Pd-C, Et ₃ N (aryl)	JOC 55 991 (1990) SL 709 (1991)
Tf ₂ O/NaBH ₄ , PPh ₃ , cat Pd(PPh ₃) ₄ (aryl)	TL 28 1381 (1987)



JACS 110 7538 (1988)



<u>X</u>	<u>Reagent(s)</u>	
OTs	SmI ₂ , MeOH	IOC 51 1136 (1986)
OMs	ThTeLi(Na)	JOC 47 3946 (1982)



<u>X</u>	<u>Reagent(s)</u>	
OMs	Na(Hg), NaH ₂ PO ₄ , MeOH	JACS 109 1564 (1987)
OTf	LiH·3H ₂ O	TL 31 3785 (1990)



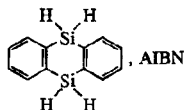
<u>Reagent</u>	<u>R</u>	
H ₂ , Raney Ni	Me, <i>p</i> -Tol	JOC 59 6318 (1994)
NaBH ₄ , NiCl ₂ ·6H ₂ O	<i>p</i> -Tol	JCS Perkin 1 1897 (1992)

9.4. Via Other Derivatives


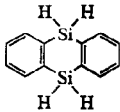



Review: Pure Appl Chem 53 15 (1981)

<u>X</u>	<u>Reducing Agent</u>	
PhC=S	<i>n</i> -Bu ₃ SnH	JCS Perkin 1 1574 (1975): 885 (1980) JOC 46 4300 (1981) (all 2° alkyl)
ClC=O	<i>n</i> -Pr ₃ SiH, (<i>t</i> -BuO) ₂	JCS Perkin 1 1207 (1980) (1°, 2° alkyl)
R'OC=S	Ph ₂ SiH ₂ , cat Et ₃ B, air <i>n</i> -Bu ₃ SnH	TL 31 4681 (1990) (2° alkyl) JCS Perkin 1 1718 (1977) (2° alkyl)
PhOC=S	Et ₃ SiH, (PhCO ₂) ₂ (Me ₃ Si) ₃ SiH, AIBN	JOC 58 249 (1993) (2° alkyl) SL 705 (1990); 595 (1992) TL 33 6629 (1992) (all 2° alkyl)
	Ph ₂ SiH ₂ , AIBN	TL 33 6629 (1992) (2° alkyl)




TL 36 3897 (1995) (2° alkyl)

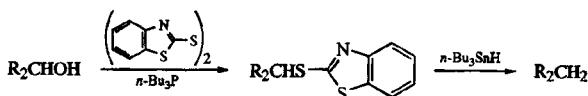
<u>X</u>	<u>Reducing Agent</u>	
	<i>n</i> -Bu ₃ SnH	JACS 103 932 (1981); 105 4059 (1983); 110 4672, 5442 (1988) (all 2° alkyl) JOC 52 3706 (1987) (2° alkyl); 55 924 (1990) (1°, 2° alkyl) TL 29 4061 (1988) (2° alkyl) TL 29 6125 (1988) (2° alkyl)
	<i>n</i> -Bu ₃ SnH, Et ₃ B	TL 29 6125 (1988) (2° alkyl)
	 -CH ₂ CH ₂ SnPh ₂ H	JOC 60 2607 (1995) (2° alkyl)
	polymer-SnR ₂ H	SL 801 (1992) (2° alkyl) JOC 56 5971 (1991) (2° alkyl)
<i>p</i> -FC ₆ H ₄ OC=S	Et ₃ SiH, (PhCO ₂) ₂	TL 32 7187 (1991) (2° alkyl) JACS 115 7166 (1993) (1° alkyl)
	PhSiH ₃ , AIBN or (PhCO ₂) ₂	SL 435 (1991) (1°, 2° alkyl)
	<i>n</i> -Bu ₃ SnH	TL 35 2587 (1994) (2° alkyl)
	(RO) ₂ P(O)H (R = Me, Et), cat (PhCO ₂) ₂	TL 33 2311 (1992) JOC 58 6838 (1993) (both 1°, 2° alkyl)
	(R ₃ NH)H ₂ PO ₂	TL 33 5709 (1992) JOC 58 6838 (1993) (both 1°, 2° alkyl)
C ₆ F ₅ OC=S	<i>n</i> -Bu ₃ SnH	TL 30 2619 (1989) (2° alkyl) JOC 59 1475 (1994) (2° α-hydroxy ketone)
	(MeO) ₂ P(O)H, cat (PhCO ₂) ₂	JOC 58 6838 (1993) (2° alkyl)
	(R ₃ NH)H ₂ PO ₂	JOC 58 6838 (1993) (2° alkyl)
2,4-Cl ₂ C ₆ H ₃ OC=S	<i>n</i> -Bu ₃ SnH	JOC 58 2977 (1993) (2° alkyl)
2,4,6-Cl ₃ C ₆ H ₂ OC=S	<i>n</i> -Bu ₃ SnH	TL 30 2619 (1989) (2° alkyl)
PhSC=S	<i>n</i> -Bu ₃ SnH	Chem Pharm Bull 26 1786 (1978) (2° alkyl)
MeSC=S	PhSiH ₃ , AIBN or (PhCO ₂) ₂	SL 435 (1991) (2° alkyl)
	Ph ₂ SiH ₂	SL 435 (1991) (2° alkyl) TL 34 2733 (1993) (3° alkyl)
	 , AIBN	TL 36 3897 (1995) (2° alkyl)
	Et ₃ SiH, (PhCO ₂) ₂	TL 32 7187 (1991) (2° alkyl)
	R ₃ SiH, cat RSH	TL 31 5093 (1990) (1°, 2° alkyl)
	(Me ₃ Si) ₃ SiH, AIBN	JOC 56 678, 912, 6538 (1991) (all 2° alkyl)
	(Me ₃ Si) ₂ SiHMe	JOC 57 3405 (1992) (2° alkyl)
	(RS) ₃ SiH	SL 219 (1990) JOC 57 2427 (1992) (both 2° alkyl)

$n\text{-Bu}_3\text{SnH}$	<p>JCS Perkin I 1574 (1975); 1718 (1977) (both 2° alkyl) Austral J Chem 30 1269 (1977) (2° alkyl) Chem Pharm Bull 26 1786 (1978) (2° alkyl) JACS 101 6116 (1979); 108 3443 (1986); 110 940 (1988); 115 12550 (1993) (all 2° alkyl) Nouv J Chim 4 59 (1980) (2° alkyl) Org Syn 64 57 (1985) (2° alkyl) JOC 51 2148 (1986) (2° alkyl); 52 1057 (2° benzylic), 3096 (2° alkyl), 4647 (2° alkyl) (1987); 56 438 (1991) (2° alkyl); 58 2530, 3798 (1993) (both 2° alkyl); 59 1475 (1994) (2° alkyl) TL 27 2679 (2° alkyl), 3057 (2° alkyl) (1986); 28 3615 (2° alkyl), 3883 (2° alkyl) (1987); 34 2733 (1993) (3° alkyl); 35 4707 (1994) (2° alkyl) CC 1351, 1802 (1987) (both 2° alkyl) Org Syn Coll Vol 7 139 (1990) (2° alkyl) TL 29 6125 (1988) (2° alkyl) JOC 57 6519 (1992); 59 1475 (1994) (both 2° alkyl) JOC 58 3046 (1993) (2° alkyl)</p>
$n\text{-Bu}_3\text{SnH}$, Et_3B Ph_3SnH	<p>SL 801 (1992) (2° alkyl) TL 33 2311 (1992) JOC 58 6838 (1993) (both 2° alkyl)</p>
$o\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{SnMe}_2\text{H}$, AIBN polymer-Sn($n\text{-Bu}$) $_2\text{H}$ (MeO) $_2\text{P}(\text{O})\text{H}$, cat (PhCO_2) $_2$	<p>TL 34 2733 (1993) (3° alkyl) TL 33 5709 (1992) (2°, 3° alkyl); 35 5055 (1994) (2° alkyl) JOC 58 6838 (1993) (2°, 3° alkyl) CC 1175 (1979) (1°, 2° alkyl) TL 28 2937 (1987) (2° alkyl)</p>
(EtO) $_2\text{P}(\text{O})\text{H}$, Et_3B , O_2 (R_2NH) H_2PO_2	<p>TL 34 3745 (1993) (1°, 2° alkyl)</p>
K, $t\text{-BuNH}_2$, 18-crown-6	<p>CC 1175 (1979) JCS Perkin I 1510 (1981) (both 1°, 2° alkyl)</p>
$\text{RNHC}\equiv\text{S}$	
$\text{R}_2\text{NC}\equiv\text{S}$	
 $\text{NC}\equiv\text{S}$	
Et_3SiH	<p>JOC 56 678 (1991) (2° alkyl)</p>
K, $t\text{-BuNH}_2$, 18-crown-6	
(Me_3Si) $_3\text{SiH}$	

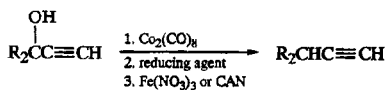
XReducing Agent

	$n\text{-Bu}_3\text{SnH}$	JCS Perkin I 1574 (1975) (1°, 2° alkyl); 1109 (1984) (2° alkyl) JOC 46 4843 (1981); 56 438 (1991) (both 2° alkyl) TL 24 865 (1983); 28 6425 (1987); 29 4077 (1988); 35 2587, 4707 (1994) (all 2° alkyl)
	$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{PPh}_3)_4$	JACS 107 2471 (1985) (2° allylic)
$\text{R}'\text{N}=\text{CNHR}'$	H_2 , cat Pd-C	Ber 107 1353 (1974) (1°, 2°, 3° alkyl; 2° benzylic)
	H_2 , cat Pd-C	Org Syn Coll Vol 6 150 (1988) (aryl)

See also page 70, Section 16.

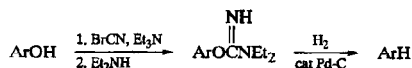


TL 27 5385 (1986)

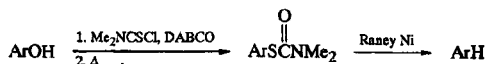


$\text{BH}_3 \cdot \text{SMe}_2$, $\text{CF}_3\text{CO}_2\text{H}$ Syn Commun 16 1535 (1986)
TL 28 1857 (1987)

NaBH_4 , $\text{CF}_3\text{CO}_2\text{H}$ JACS 107 4999 (1985)



Ber 107 1213 (1974)
JOC 59 6318 (1994)



JOC 59 6318 (1994)

10. Sulfur Compounds

Reviews:

- E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Chemical Publishing Co., New York (1958), Vol 1, p 115 (Raney Ni)
 N. Kharasch and C. Y. Meyers, "The Chemistry of Organic Sulfur Compounds," Pergamon Press, New York (1966), Vol 2, p 35 (Raney Ni)
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 4.3, p 835

See also page 47, Section 9.3 and page 49, Section 9.4, for reduction of sulfur-containing derivatives of alcohols and phenols and page 229, Section 4, for reduction of allylic sulfonates and sulfones with double bond transposition.



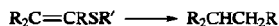
R_2CHMgX , cat $\text{NiCl}_2\text{-PPh}_3$ (R = aryl)	CC 840 (1982)
Mo(CO)_6 , HOAc or SiO_2 (R = alkyl, aryl)	CC 169 (1980)
P(OEt)_3 , h ν (R = 1° alkyl, benzyl)	JACS 78 6414 (1956)
NaH , Ni(OAc)_2 , <i>t</i> -AmOH (R = 1° alkyl, aryl)	JOC 54 4848 (1989)
NaBH_4 , $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$ (R = 1°, 2° alkyl)	JOC 58 2407 (1993)
LiAlH_4 , nickelocene (R = 1°, 3° alkyl; aryl)	JOC 53 4466 (1988)
LiAlH_4 , $\text{NiBr}_2\cdot\text{DME}$, PPh_3 (R = 1°, 3° alkyl; aryl)	JOC 54 4474 (1989)



Raney Ni	TL 28 1799 (1987); 33 5567 (1992); 36 1223 (1995)
NaH , Ni(OAc)_2 , <i>t</i> -AmOH	JOC 54 4848 (1989)
NaBH_4 , $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$	JOC 58 2407 (1993)
LiAlH_4 , nickelocene	JOC 53 4466 (1988)
LiAlH_4 , $\text{NiBr}_2\cdot\text{DME}$, PPh_3	JOC 54 4474 (1989)



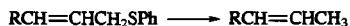
Raney Ni	TL 26 39 (1985); 28 1459 (1987) JOC 55 5589 (1990)
NaH , Ni(OAc)_2 , <i>t</i> -AmOH, (bipy)	JOC 54 4848 (1989)
NaBH_4 , $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$	Org Syn Coll Vol 7 476 (1990) JOC 58 2407 (1993)
NaBH_4 , $\text{CoCl}_2\cdot 6\text{H}_2\text{O}$	JOC 58 2407 (1993)
LiAlH_4 , $\text{NiBr}_2\cdot\text{DME}$, PPh_3	JOC 54 4474 (1989)
$\text{R}'_2\text{CHMgX}$, cat $\text{NiCl}_2\text{-PPh}_3$ (R = Me)	CC 840 (1982)
AlCl_3 , EtSH (R = Et, <i>i</i> -Pr; Ar = polycyclic)	TL 23 689 (1982)



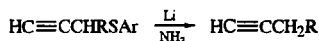
NaBH₄, NiCl₂·6H₂O JOC 58 2407 (1993)
 LiAlH₄, TiCl₄ CL 291 (1973)



Raney Ni JACS 73 1528 (1951)
 NaH, Ni(OAc)₂, *t*-AmOH, bipy JOC 55 6194 (1990)
 R₂CHMgX, cat NiCl₂-PPh₃ TL 22 3463 (1981)
 CC 840 (1982)



Li, NH₃ JACS 103 4615 (1981)
 TL 24 5531 (1983)
 Li, EtNH₂ TL 3707 (1969)
 Tetr 27 5861 (1971)
 Proc Natl Acad Sci USA 68 1294 (1971)
 JACS 95 4444 (1973)
 Syn 129 (1974)
 JOC 45 4097 (1980)
 Na, *i*-PrOH, THF TL 28 5665 (1987)
 LiHBEt₃, cat Pd(PPh₃)₄ JOC 47 4380 (1982)



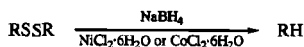
JOC 46 5041 (1981)



Li, NH₃ JOC 57 4590 (1992)
 Li, NH₃, *t*-BuOH JOC 54 5039 (1989)
 Ca, NH₃ JOC 55 5966 (1990)
 Raney Ni Tetr 37 4027 (1981)
 Syn 937 (1982)
 JACS 112 5276 (1990)
 JOC 57 2084 (1992); 58 2173 (1993)
 NaH, Ni(OAc)₂, *t*-AmOH, (bipy) JOC 54 4848 (1989)
 NaBH₄, CoCl₂·6H₂O JOC 58 2407 (1993)
 NaBH₄, NiCl₂·6H₂O JOC 58 2407 (1993)
 LiAlH₄, TiCl₄ CL 291 (1973)
 LiAlH₄, NiBr₂·DME, PPh₃ JOC 54 4474 (1989)
 LiAlH₄, CuCl₂ BCSJ 44 2285 (1971)



NaH, Ni(OAc)₂, *t*-AmOH, (bipy or PPh₃) JOC 54 4848 (1989)
 LiAlH₄, TiCl₄ CL 291 (1973)
 Mo(CO)₆, SiO₂ Pure Appl Chem 52 607 (1980)



R = alkyl, aryl

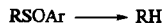
JOC 58 2407 (1993)



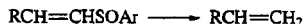
Raney Ni SL 194, 197 (1992)
 NaH, Ni(OAc)₂, *t*-AmOH TL 29 2963 (1988)
 JOC 55 6194 (1990)
 NaBH₄, NiCl₂·6H₂O JOC 58 2407 (1993)
 LiAlH₄, nickelocene JOC 53 4466 (1988)
 LiAlH₄, NiBr₂·DME, PPh₃ JOC 54 4474 (1989)



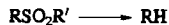
NaH, Ni(OAc)₂, *t*-AmOH, bipy JOC 55 6194 (1990)
 R₂CHMgX, cat NiCl₂·PPh₃ CC 840 (1982)



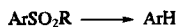
Al(Hg) JOC 46 5244 (1981)
 Raney Ni CC 1688 (1986)
 JOC 55 2128 (1990); 56 2317 (1991)
 SL 167 (1992)



Raney Ni JACS 73 1528 (1951)
 NaH, Ni(OAc)₂, *t*-AmOH JOC 55 6194 (1990)
t-BuLi, MeOH JOC 55 741 (1990)



NaH, Ni(OAc)₂, ROH TL 29 2963 (1988)
 JOC 55 6194 (1990)
 LiAlH₄, NiBr₂·DME, PPh₃ JOC 54 4474 (1989)
 Al(Hg), H₂O, THF JOC 54 2247 (1989)



NaH, Ni(OAc) ₂ , <i>t</i> -AmOH	JOC 55 6194 (1990)
R ₂ CHMgX, cat NiCl ₂ -PPh ₃	CC 840 (1982)

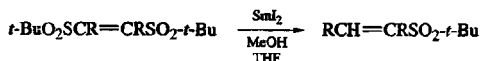


Li, EtNH ₂	JOC 39 2135 (1974) BSCF 513 (1976) JCS Perkin I 761 (1981) CL 25, 1711 (1981) JACS 107 686 (1985)
Li, EDA	BSCF 513 (1976) Tetr 37 1233 (1981)
Li, <i>t</i> -BuOH, Na ₂ HPO ₄ , THF, HMPA	JOC 53 1922 (1988)
Li, naphthalene	JOC 58 5892 (1993)
Na(Hg), MeOH, (phosphate)	JCS 4881 (1952) JOC 38 2747 (1973); 51 5100 (1986); 53 5389 (1988) BSCF 3065 (1973); 1363 (1975); 513, 525 (1976) TL 3477 (1976); 28 813 (1987); 31 3279 (1990) JACS 102 853 (1980); 106 3811 (1984); 107 2033 (1985); 108 1035 (1986); 109 6205 (1987); 111 7487 (1989) JCS Perkin I 761 (1981) Syn 55 (1981) CC 451 (1986)
Na, EtOH	CL 2105 (1984) TL 27 4817 (1986)
Mg, MeOH	JOC 53 1823 (1988)
Mg, cat HgCl ₂ , EtOH	TL 34 4541 (1993)
Raney Ni	BSCF 525 (1976)
SmI ₂ , HMPA	TL 32 1949 (1991)
LiHAl(O- <i>t</i> -Bu) ₃	TL 34 3051 (1993)

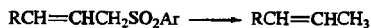


Na(Hg), Na ₂ HPO ₄ , MeOH	TL 27 2187 (1986); 32 4583 (1991) JOC 56 5834 (1991)
Mg, cat HgCl ₂ , EtOH	TL 34 4541 (1993)
Al(Hg), H ₂ O	CC 351 (1973)
SmI ₂ , MeOH	JOC 60 5770 (1995)
NaH, Ni(OAc) ₂ , <i>t</i> -AmOH	JOC 55 6194 (1990)

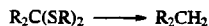
LiAlH ₄ , CuCl ₂	CC 351 (1973)
<i>n</i> -BuMgCl, cat Ni(acac) ₂	TL 28 6273 (1987)
RMgX (R = <i>i</i> -Pr, <i>n</i> -Bu), Ni or Pd catalyst	TL 24 4311 (1983)
EtMgBr, cat Pd(acac) ₂	TL 32 4583 (1991)
	JOC 60 5770 (1995)
SmI ₂	TL 34 2003 (1993)
	JOC 60 3194 (1995)
Na ₂ S ₂ O ₄ , H ₂ O	TL 23 3265 (1982); 36 4833 (1995)
	Tetr 42 2469, 2475 (1986)
	JOC 55 247 (1990); 57 584 (1992)



TL 32 4579 (1991)

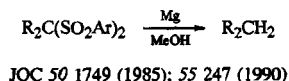


Li, EtNH ₂	JOC 39 2135 (1974)
	BSCF 513 (1976)
	JCS Perkin I 761 (1981)
	CL 25 (1981)
Li, EDA	BSCF 513 (1976)
Na, 1,8-dimethylaminonaphthalene	TL 32 1149 (1991)
Na, EtOH	BCSJ 55 1325 (1982)
Na(Hg), CH ₃ OH	BSCF 513 (1976)
Na(Hg), CH ₃ OH, Na ₂ HPO ₄	TL 3477 (1976)
	JCS Perkin I 761 (1981)
	JOC 51 5100 (1986)
Mg, MeOH	JOC 56 454 (1991)
Mg, cat HgCl ₂ , EtOH	TL 34 4541 (1993)
LiHBEt ₃ , cat Pd(PPh ₃) ₄	JOC 47 4380 (1982)
LiHBEt ₃ , cat PdCl ₂ (dppp)	SL 763 (1994)




Li, EtNH ₂	JCS 4413 (1960)
Na, NH ₃ , EtOH	JACS 80 4604 (1958)
	TL 29 147 (1988)
	JOC 56 3102 (1991)

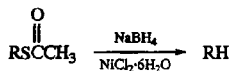
Raney Ni	JACS 66 909 (1944); 84 2938 (1962); 109 3025 (1987); 110 1901, 6210 (1988) Can J Chem 37 1870 (1959) Org Rxns 12 356 (1962) Chem Rev 62 347 (1962) JOC 33 3551 (1968); 50 2359, 2607 (1985); 52 2875, 3346 (1987); 53 3852 (1988); 55 1569 (1990); 57 4444 (1992); 58 3840 (1993); 59 5999 (1994)
NaH, Ni(OAc) ₂ , <i>t</i> -AmOH	TL 29 2963 (1988) JOC 55 6194 (1990)
NaBH ₄ , NiCl ₂ ·6H ₂ O	JOC 59 5999, 7934 (1994)
LiAlH ₄	JACS 86 478 (1964)
LiAlH ₄ , TiCl ₄	CL 291 (1973)
LiAlH ₄ , nickelocene	JOC 53 4466 (1988)
LiAlH ₄ , CuCl ₂	BCSJ 44 2285 (1971)
LiAlH ₄ , CuCl ₂ , ZnCl ₂	Int J Sulfur Chem 7 173 (1972) Org Syn Coll Vol 6 109 (1988)
<i>n</i> -Bu ₃ SnH, AIBN	JOC 45 3393 (1980)
N ₂ H ₄ , KOH	JACS 81 5834 (1959)
P ₂ L ₄ , CH ₂ Cl ₂	TL 30 1277 (1989)



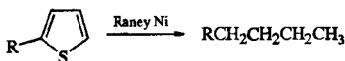
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
SR	F COR	Na, EtOH	TL 29 6851 (1988)
		Li, NH ₃ /H ₂ O	Syn Commun 3 265 (1973)
		Na(Hg), Na ₂ HPO ₄ , MeOH	TL 3477 (1976)
		Zn, NH ₄ Cl, H ₂ O	JOC 52 2317 (1987)
		Zn, Me ₃ SiCl	Syn Commun 7 427 (1977)
		Raney Ni	Syn Commun 3 265 (1973)
			JOC 47 4384 (1982); 50 2589 (1985); 54 3449 (1989)
			CC 717 (1985)
		NaH, Ni(OAc) ₂ , <i>t</i> -AmOH	JOC 54 4848 (1989)

		LiAlH ₄ , nickelocene	JOC 53 4466 (1988)
		SmI ₂ , MeOH	JOC 51 1135 (1986)
		NaSR	BCSJ 44 828 (1971)
		PhSH, DMBI	JOC 57 662 (1992)
		ThTeLi(Na)	JOC 47 3946 (1982)
	CO ₂ R	Li, NH ₃ /H ₂ O	Syn Commun 3 265 (1973)
		Raney Ni	CC 717 (1985)
		JOC 57 4991 (1992)	
		NaSR	BCSJ 44 828 (1971)
		<i>n</i> -Bu ₃ SnH	TL 29 6943 (1988); 36 5007 (1995)
	CONR ₂	Raney Ni	JOC 57 4765 (1992)
		SL 907 (1993)	
	CONRCOR	<i>n</i> -Bu ₃ SnH	JACS 116 82 (1994)
	CN	Li, naphthalene/H ₂ O	Syn Commun 3 265 (1973)
	CO ₂ R, SO ₂ Ph	Zn, HOAc	TL 36 7243 (1995)
SOPh	COR	Al(Hg), H ₂ O	JACS 87 1345 (1965); 103 2886 (1981); 104 4180 (1982); 114 974 (1992)
		JOC 46 5244 (1981)	
		TL 30 3853 (1989); 34 5341 (1993)	
		<i>n</i> -Bu ₃ SnH	JOC 60 7778 (1995)
		Zn, NH ₄ Cl, H ₂ O	JOC 52 2317 (1987)
		SmI ₂ , MeOH	JOC 51 1135 (1986)
	CO ₂ R	Al(Hg), H ₂ O	JACS 103 2886 (1981)
SO ₂ Ph	COR	Li, NH ₃	JOC 56 7071 (1991)
		Na(Hg), Na ₂ HPO ₄ , MeOH	JOC 54 3347, 3755 (1989); 60 3580 (1995)
		JACS 112 5583 (1990)	
		Mg, cat HgCl ₂ , EtOH	TL 34 4541 (1993)
		Al(Hg), H ₂ O	JACS 87 1345 (1965)
		JOC 45 4002 (1980); 49 1246 (1984); 54 3496, 3755 (1989)	
		TL 34 5343 (1993)	
		SL 249 (1995)	
		TL 28 5017 (1987)	
		MeOH	SL 793 (1992)
		NaBH ₃ CN, <i>n</i> -Bu ₃ SnCl	SL 973 (1995)
		LiAlH ₄ , nickelocene	JOC 53 4466 (1990)
		<i>n</i> -Bu ₃ SnH	TL 30 1037, 5579 (1989)

<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
SO ₂ Ph (<i>continued</i>)	COR (<i>continued</i>)	Zn, HOAc	TL 32 7727 (1991)
		SmI ₂ , MeOH	JOC 51 1135 (1986)
			TL 36 3577 (1995)
	CO ₂ R	SmI ₂ , THF	SL 249 (1995)
		PhSH, DMBI	JOC 57 662 (1992)
		Na(Hg), Na ₂ HPO ₄ , MeOH	TL 3477 (1976)
		Mg, cat HgCl ₂ , ROH	TL 34 4541 (1993)
			SL 1127 (1995)
		Al(Hg), H ₂ O, THF	JOC 54 2247 (1989)
			TL 34 2945 (1993)
	CONR ₂	SmI ₂	TL 35 4603 (1994)
			JOC 60 5048 (1995)
		Al(Hg), H ₂ O	JACS 87 1345 (1965)
	CN	SmI ₂ , MeOH, H ₂ O	TL 36 2531 (1995)
SO ₂ Ph NO ₂		Mg, cat HgCl ₂ , MeOH	TL 36 5691 (1995)
		LiC ₁₀ H ₈ /H ₂ O	TL 35 5437 (1994)
		DMBI	JOC 53 3897 (1988)
		1-benzyl-1,4-dihydro-nicotinamide, hv	JOC 46 765 (1981)
		NaTeH	BCSJ 58 1067 (1985)



JOC 58 2407 (1993)



Org Rxs 12 393 (1962)

JOC 51 5221 (1986); 57 2052 (1992)

11. Selenium Compounds

See also page 67, Section 12.7.

R' = Me, CH₂Ar, ArLi, EtNH₂

TL 2643 (1976)

Raney Ni


TL 2643 (1976)

Can J Chem 55 3894 (1977)

JACS 99 3185 (1977)

JCS Perkin I 1682 (1978); 1237 (1984)

CC 1252 (1982)

Raney Ni, H ₂	JACS 102 3784 (1980)
NaBH ₄ , NiCl ₂ ·6H ₂ O	JCS Perkin I 1682 (1978) TL 23 4949 (1982); 26 4187 (1985) CC 1417 (1984) JOC 53 3815 (1988)
(Me ₃ Si) ₃ SiH	JOC 56 678 (1991)
(RS) ₃ SiH	SL 219 (1990) JOC 57 2427 (1992)
(Me ₃ Si) ₂ SiHMe	JOC 57 3405 (1992)
n-Bu ₃ SnH	TL 1023 (1978) Prostaglandins 16 789 (1978) JACS 101 3704 (1979); 102 3784 (1980) SL 269 (1992) JOC 57 4457 (1992)
n-Bu ₃ SnH, Et ₃ B	JOC 55 1418 (1990); 57 3887 (1992)
Ph ₃ SnH	CC 41, 441 (1978) JACS 102 4438 (1980) JOC 56 3425 (1991)
 CH ₂ CH ₂ SnPh ₂ H	JOC 60 2607 (1995)
$\text{C}=\text{C}-\text{C}-\text{SeAr} \longrightarrow \text{C}=\text{C}-\text{C}-\text{H}$	
NaBH ₄ , NiCl ₂ ·6H ₂ O	CC 1417 (1984) JOC 53 3815 (1988)
LiHBEt ₃ , cat Pd(PPh ₃) ₄	JOC 47 4380 (1982)
$\text{R}_2\text{C}(\text{SeR}')_2 \longrightarrow \text{R}_2\text{CH}_2$	
Li, EtNH ₂	TL 2643 (1976)
Raney Ni	TL 2643 (1976)
Ph ₃ SnH	JACS 102 4438 (1980) TL 22 1623 (1981)

12. Aldehydes and Ketones

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Parts 1.13 and 1.14, pp 307-362

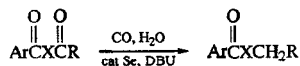
12.1. Direct Reduction



H₂, various catalysts (aryl aldehydes and ketones) Org Rxn 7 263 (1953)
R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York (1965)

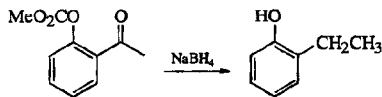
H ₂ , cat Pd-C (aryl aldehydes and ketones)	JOC 36 737 (1971); 53 904, 3761 (1988); 57 6716 (1992); 58 4871, 7149 (1993); 59 878 (1994) Can J Chem 49 2712 (1971) Tetr 38 3555 (1982) Syn 940 (1982)
D ₂ , cat Pd-C, DOAc (aryl ketones)	JOC 52 2938 (1987)
H ₂ , cat Pt-C (aryl aldehyde)	JOC 60 5717 (1995)
H ₂ , cat PtO ₂ (aryl ketones)	TL 23 2415 (1982)
(NH ₄)O ₂ CH, cat Pd-C, HOAc (aryl aldehydes and ketones)	TL 29 3741 (1988)
cyclohexene or limonene, cat Pd-C, FeCl ₃ (aryl aldehydes and ketones)	CC 757 (1976)
Raney Ni, aq EtOH (aryl aldehydes and ketones)	JOC 7 587 (1942) TL 21 2637 (1980)
CO, H ₂ O, cat Se, DBU (aryl ketones)	JOC 53 1326 (1988)
HI, P (diaryl ketone)	JOC 13 786 (1948)
HI, P, I ₂ (aryl ketones)	Ber 92 1705 (1959) Can J Chem 52 1229 (1974) JOC 57 4074 (1992)
(<i>i</i> -PrO) ₃ P	SL 54 (1990)
Li, NH ₃ /NH ₄ Cl (aryl ketones)	JOC 36 2588 (1971)
Li, cat (4- <i>t</i> -BuC ₆ H ₄) ₂ , ultrasound (aryl ketones)	TL 30 4931 (1989)
Zn, HOAc, (H ₂ O), ultrasound	TL 34 361 (1993)
Zn, HCl	CC 919 (1969) Org Syn Coll Vol 6 289 (1988)
Zn, HCl, H ₂ O	Org Rxns 1 155 (1942) (review) JACS 76 6368 (1954) Angew 71 726 (1959) Quart Rev 23 522 (1969) CC 893 (1986) (mechanism)
Zn, HCl, HgCl ₂ , H ₂ O	JOC 55 3537 (1990); 59 4495 (1994)
Zn, HCl, Ac ₂ O	JCS C 2887 (1968)
Zn, NaOH or KOH (diaryl ketones)	JOC 51 3502 (1986); 52 3205 (1987)
Zn(Hg), HCl (aryl ketones)	JACS 69 1254 (1947)
Zn(Hg), HCl, HOAc	JOC 56 1052 (1991)
BH ₃ (diaryl ketone)	J Sci Ind Res B 21 583 (1962) JACS 116 7072 (1994)
BH ₃ , BF ₃ ·OEt ₂ (cyclopropyl and aryl ketones)	TL 1849 (1967)

$\text{BH}_3\cdot\text{py}$, $\text{CF}_3\text{CO}_2\text{H}$ (aryl ketones)	Chem Pharm Bull 27 2405 (1979)
$\text{BH}_3\cdot t\text{-BuNH}_2$, AlCl_3 (aryl ketones)	JOC 54 491, 4350 (1989)
NaBH_4 , $\text{CF}_3\text{CO}_2\text{H}$ (aryl ketones)	Syn 763 (1978) JOC 50 5451 (1985); 54 4350 (1989)
NaBH_4 , $\text{BF}_3\cdot\text{OEt}_2$ (aryl ketones)	Proc Chem Soc 357 (1962) J Sci Ind Res B 21 583 (1962)
NaBH_4 , AlCl_3 (diaryl ketone)	J Sci Ind Res B 21 583 (1962)
NaBH_4 , PdCl_2 (aryl ketones)	CL 1029 (1981)
NaBH_3CN , $\text{BF}_3\cdot\text{OEt}_2$	SL 93 (1995) (aryl aldehydes and ketones) TL 36 2347 (1995) (enal, enones)
NaBH_3CN , ZnI_2 (aryl aldehydes and ketones)	JOC 51 3038 (1986) TL 35 4759 (1994)
$t\text{-Bu}_2\text{AlH}$, AlBr_3 (aryl ketones)	JOC 57 2143 (1992)
LiAlH_4 , AlCl_3 (enones, aryl ketones)	JCS 3755 (1957); 1406 (1960); 1405 (1961); 1658 (1962) JACS 80 2896 (1958) Tetr 21 2641 (1965) TL 28 2937 (1987) JOC 55 3409 (1990); 57 7118 (1992)
$\text{Me}_3\text{Si}(\text{OSiHMe})_n\text{OSiMe}_3$, AlCl_3 (aryl ketones)	JCS Perkin I 1705 (1989)
Et_3SiH , BF_3 (ketones, aryl aldehydes)	JOC 43 374 (1978) Org Syn 60 108 (1981) Org Syn Coll Vol 7 393 (1990)
Et_3SiH , $\text{BF}_3\cdot\text{OEt}_2$ (enone, aryl ketone)	JOC 52 1984 (1987) TL 35 2071 (1994)
Et_3SiH , AlCl_3 (aryl ketones)	JCS Perkin I 1705 (1989)
Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$ (aryl aldehydes and ketones)	Bull Acad Sci USSR, Div Chem Sci 1245 (1966) Tetr 23 2235 (1967) JOC 38 2675 (1973); 54 1548 (1989); 55 2694 (1990); 59 1184 (1994) Syn 633 (1974) (review) TL 34 7447 (1993)
Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$, NH_4F (aryl ketones)	SL 647 (1992)
PhSiMe_2H , $\text{CF}_3\text{CO}_2\text{H}$ (aryl aldehydes)	JOC 38 2675 (1973)

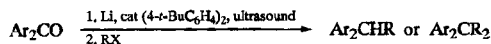


X = —, CHR

TL 33 6347 (1992)

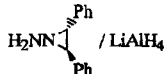


TL 36 5335 (1995)



TL 31 6155 (1990)

12.2. Via Hydrazones

- NH_2NH_2 , $\text{HOCH}_2\text{CH}_2\text{OH}$ JOC 54 1485 (1989)
- NH_2NH_2 , K_2CO_3 , $(\text{HOCH}_2\text{CH}_2)_2\text{O}$ JACS 105 7352, 7358 (1983); 106 6690, 6702 (1984)
 JOC 58 556 (1993)
- NH_2NH_2 , K_2CO_3 , $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_3\text{H}$ JOC 48 1404 (1983)
- NH_2NH_2 , KOH , $\text{HOCH}_2\text{CH}_2\text{OH}$ Org Rxns 4 378 (1948)
 JACS 71 3301 (1949); 107 7978 (1985);
 108 3385 (1986)
 JCS 2056 (1955)
 Angew Int 7 120 (1968)
- NH_2NH_2 , $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$ ($n = 2$ or 3),
 NaOH or KOH JACS 68 2487 (1946); 110 4652 (1988)
 Ind J Chem 2 229 (1964)
 JOC 50 2359 (1985); 52 3205 (1987)
- NH_2NH_2 , $\text{KO-}t\text{-Bu}$ JOC 51 5019 (1986)
-  / LiAlH_4 TL 32 1691 (1991)
- TsNHNH_2 / BH_3 BCSJ 47 2323 (1974)
- TsNHNH_2 / CB / $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ JOC 40 1834 (1975); 53 3761 (1988); 57 2888 (1992); 59 4186 (1994)
 Syn 124 (1977)
 JACS 107 5732 (1985)
- TsNHNH_2 / CB / MeOH / $n\text{-Bu}_4\text{NOAc}$ Syn Commun 9 275 (1979)
 JOC 57 4598 (1992)
- TsNHNH_2 / $(\text{PhCO}_2)_2\text{BH}$ / $\text{NaOAc} \cdot 3\text{H}_2\text{O}$ JOC 46 1217 (1981)
- TsNHNH_2 / $(\text{PhCO}_2)_2\text{BH}$ / NaOH JACS 107 1721 (1985)
- TsNHNH_2 / NaBH_4 Chem Ind 153, 1689 (1964)
 Ber 98 3236 (1965)
 Org Syn 52 122 (1972)
 BCSJ 47 2323 (1974)
 TL 28 4759 (1987)
 Org Syn Coll Vol 6 62 (1988)

$\text{TsNHNH}_2 / \text{NaBH}_3\text{CN}$ (aliphatic aldehydes and ketones only)

JACS 93 1793 (1971); 95 3662 (1973); 106 2115 (1984); 109 7270 (1987)
Syn 35 (1975)
Org Prep Proc Int 11 201 (1979)
JOC 50 2607 (1987)

$\text{TsNHNH}_2 / \text{NaBH}_3\text{CN}, \text{ZnCl}_2$ (aliphatic aldehydes and ketones only)

JOC 50 1927 (1985)
JACS 115 1676 (1993)

$\text{TsNHNH}_2 / \text{LiAlH}_4$

Tetr 19 1127 (1963); 22 487 (1966)
Ber 98 3236 (1965)

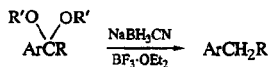
$\text{TsNHNH}_2 / i\text{-Bu}_2\text{AlH}$

JOC 53 1969 (1988)

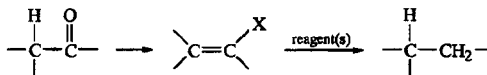
2,4,6-($t\text{-Pr}$) $_3\text{C}_6\text{H}_2\text{SO}_2\text{NHNH}_2 / \text{CuBH}_4(\text{PPh}_3)_2$

TL 21 4031 (1980)

12.3. Via Oxygen and Sulfur Derivatives



SL 93 (1995)



X

OSO_2CF_3

Reagents

H_2 , cat Pd-C

TL 23 117 (1982)
JOC 57 4103 (1992); 58 5035 (1993); 60 711 (1995)
JACS 115 8851 (1993)
JACS 111 4852 (1989)
JOC 59 332 (1994)

H_2 , cat PtO_2

$\text{OPO}(\text{OEt})_2$

H_2 , cat Pt-C

Li, $t\text{-BuOH}$, EtNH_2

JACS 104 2198 (1982)
JACS 108 5650 (1986)



See page 53, Section 10.

12.4. Via Selenium Derivatives



See page 60, Section 11.

12.5. Decarbonylation



Reviews:

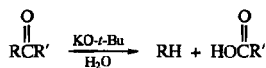
Syn 157 (1969)

H. M. Colquhoun, D. J. Thompson, M. V. Twigg, "Carbonylation - Direct Synthesis of Carbonyl Compounds," Plenum, New York (1991), Chpt 11

Reagent(s)	R	
hv, K ₂ CO ₃ , EtOH	alkyl	JACS 111 8834, 8842 (1989)
R'SH, hv	alkyl	JACS 85 4010 (1963)
Fe(CO) ₅	vinyl	TL 447 (1973)
cat Ru(tpp)(PPh ₃) ₂ , n-Bu ₃ P	alkyl, aryl	CC 939 (1980)
cat Rh-Al ₂ O ₃	alkyl	TL 33 6135 (1992)
cat ClRh(PPh ₃) ₃	alkyl, aryl, vinyl	TL 3969 (1965); 4113 (1966); 2173 (1967); 1899 (1968); 2145 (1969); 823 (1970); 28 5669 (1987) CC 129 (1966); 856 (1974) JACS 89 2338 (1967); 90 99 (1968); 93 5465 (1971); 95 1229, 2038, 7862 (1973); 106 1421, 5312, 6364 (1984); 110 6914 (1988); 112 3018, 3156 (1990); 114 9401 (1992) JCS A 348 (1968); 612 (1969) JOC 41 2288 (1976); 45 315 (1980); 49 621 (1984); 52 3303 (1987); 54 5257 (1989); 57 5370, 5712 (1992) JCS Perkin I 700 (1977) Izv Akad Nauk SSSR, Ser Khim 655 (1983)
cat ClRh(PPh ₃) ₃ , N ₃ PO(OPh) ₂	alkyl, vinyl	JOC 57 5075 (1992)
cat ClRh(Ph ₂ PCH ₂ CHRPPh ₂) ₂ (R = H, Me)	aryl	JACS 100 7083 (1978) Fund Res Homogeneous Catal 3 909 (1979) JOC 49 3195 (1984)
cat ClRh(CO)(PPh ₃) ₂ , dppp	alkyl aryl	TL 28 6089 (1987) JOC 49 3195 (1984) TL 34 1987 (1993)
cat [ClRh(CO)(PMe ₃) ₂]	alkyl	JACS 114 2520 (1992)
cat Pd-C	alkyl, aryl	JOC 25 2215 (1960); 52 1201 (1987)

12.6. Ketone Cisavage

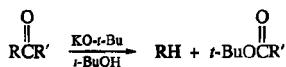
Review: Org Prep Proc Int 22 167 (1990) (Haller Bauer reaction)



JCS 1408 (1948)

JACS 89 946 (1967)

JCS C 455 (1971)



JACS 109 6858 (1987)

JOC 53 4972, 4978 (1988); 54 5044, 5054 (1989)

NaNH₂

Org Rxs 9 1 (1957) (review)

JOC 36 2937 (1971); 54 1399, 1408 (1989)

NaNH₂, DABCO

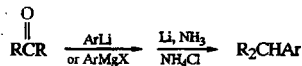
Syn 395 (1975)

MNH₂ (M = Li, Na, K)

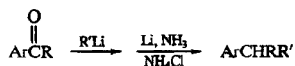
JACS 109 6858 (1987)

JOC 53 4972, 4978 (1988); 54 5044, 5054 (1989)

12.7. Reductive Coupling



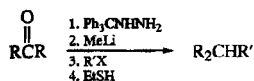
JOC 40 271, 3306 (1975); 41 3465 (1976); 46 4139, 5060 (1981)



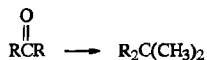
JOC 38 1735, 1738 (1973); 41 1494 (1976)

Org Syn 55 7 (1976)

Org Syn Coll Vol 6 537 (1988)



CC 22 (1984)

 $(\text{CH}_3)_3\text{Al}$

JOC 35 532 (1970)

CC 595 (1972)

 $(\text{CH}_3)_2\text{TiCl}_2$ or $(\text{CH}_3)_2\text{TiCl}_2\text{-TiCl}_4$ or $(\text{CH}_3)_2\text{Zn}$

CC 237 (1981)

JOC 48 254 (1983)

 $(\text{CH}_3)_2\text{Zn, TiCl}_4$

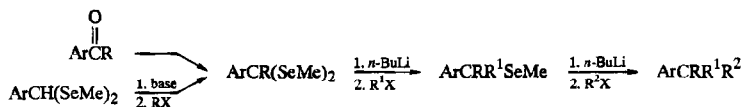
JOC 50 5727 (1985) (enone)



JOC 48 254 (1983)

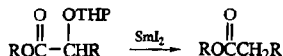
 $\text{Ar} = p\text{-ClC}_6\text{H}_4$

JOC 38 2747 (1973)



TL 27 1719, 1723 (1986)

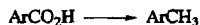
13. Acetals



TL 30 2945 (1989)

14. Carboxylic Acids

See also page 70, Section 16.

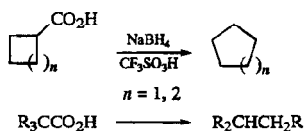
 $\text{BH}_3\cdot\text{SMe}_2$

TL 32 2759 (1991)

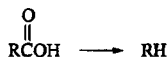
 $\text{HSiCl}_3/\text{R}_3\text{N}/\text{KOH}$

JACS 92 3232 (1970)

Org Syn Coll Vol 6 747 (1988)



JOC 54 1452 (1989)



hv (R = ArCONRCHR)

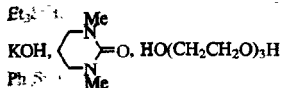
Syn 141 (1982)

hv, *t*-BuSH, *N*-aromatics

TL 30 6733 (1989)

R₂CO (RCO₂H = 2-aminoalkanoic acid)

Heterocycles 6 1167 (1977)

Et₃NKOH, HO(CH₂CH₂O)₃H

TL 35 4501 (1994)

Ph₂N

JOC 60 1319 (1995)

Ba(OH)₂ (R = indole)

JOC 60 1800 (1995)

KF, triglyme

JOC 57 4749 (1992)

quinoline, microwave irradiation

JOC 58 5558 (1993)

Cu, quinoline (R = ArCH=CH)

Org Syn Coll Vol 4 732 (1963)

Cu chromite, quinoline (R = heterocyclic)

TL 27 3045 (1986)

JOC 58 5558 (1993)

Cu₂O (R = stabilized carbanion)

Tetr 40 3229 (1984)

Cu₂O, quinoline

SL 40 (1993)

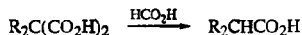
H₂, cat Ni or Pd (R = 1°, 2°, 3° alkyl; aryl)

Ber 115 808 (1982)

PhOPOCl₂/PhSeH, Et₃N/*n*-Bu₃SnH

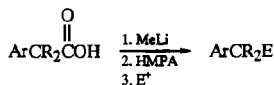
JACS 107 3285 (1985)

(R = 2-tetrahydrofuryl)

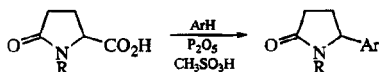


TL 35 2275 (1994)

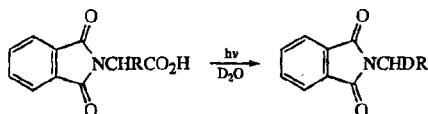
See also page 1724, Section 2 for decarboxylation of malonate esters.

E⁺ = H⁺, MeI, RSSR, Me₃SiCl

TL 29 4505 (1988)



TL 30 7057 (1989)



SL 931 (1994)

15. Acid Halides

See also page 70, Section 16.

 $n\text{-Pr}_3\text{SiH}$, $(t\text{-BuO})_2$

JCS Perkin I 1137 (1979)

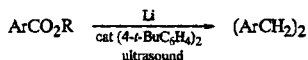
 $(\text{Me}_3\text{Si})_3\text{SiH}$, AIBN

TL 33 1787 (1992)

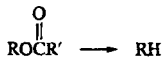
16. Esters and Lactones



JOC 44 2185 (1979)



TL 30 4931 (1989)

 $h\nu$, 1HF , H_2O ($\text{R}' = m\text{-CF}_3\text{C}_6\text{H}_4$)

JACS 115 7152 (1993)

 $h\nu$, N -methylcarbazole ($\text{R}' = \text{Ar}$; $\text{R} = 2^\circ$ alkyl)

JACS 108 3115 (1986)

 Li , NH_3 /EtOH ($\text{R} = \text{benzylic}$)

JOC 52 4879 (1987)

 Li , EtNH_2 ($\text{R} = \text{hindered alkyl, allylic}$)

JCS 1969 (1957)

CC 68 (1978); 1173 (1979)

JACS 106 723 (1984)

TL 27 5471 (1986)

 Li , EDA

Ind J Chem B 18 179 (1979)

 Na , $t\text{-BuOH}$, HMPA

CC 567 (1978)

 K , $t\text{-BuNH}_2$, 18-crown-6

CC 1173 (1979)

 Na-K , tris(3,6-dioxahexyl)amine

TL 28 2503 (1987)

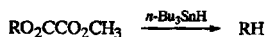
 Zn , HOAc ($\text{R} = 4\text{-acetoxyl-2-alken-5-olide}$)

TL 29 1255 (1988)

 Zn , HOAc, THF ($\text{R} = 3^\circ$ allylic, $\text{R}' = \text{CF}_3$)

JACS 109 6187 (1987)

Zn-Cu (R = 4-acetoxy-2-alken-5-olide)	TL 26 5203 (1985)
HI, H ₃ PO ₂ (R = aryl)	TL 36 1213 (1995)
Raney Ni, EtOH (R = 3° benzylic)	JACS 89 4233 (1967)
H ₂ , cat Pd-C (R = 2°, 3° benzylic)	JACS 89 4233 (1967) JOC 55 3767 (1990)
H ₂ , cat Pd-C, HClO ₄ (R = benzylic)	Syn Commun 12 983 (1982)
cat Pd(OH) ₂ -C, cyclohexene (R = allylic)	TL 30 1405 (1989)
H ₂ , cat Pt-C	JACS 89 4233 (1967) TL 32 4963 (1991)
H ₂ , cat PtO ₂	TL 32 4963 (1991)
NaBH ₃ CN, BF ₃ ·OEt ₂ (R = benzylic)	SL 93 (1995)
Et ₃ SiH, CF ₃ CO ₂ H (R = benzylic)	JACS 115 8873 (1993)
Et ₃ SiH, LiClO ₄ (R = 2° allylic)	TL 35 61 (1994)
Ph ₃ SiH, (t-BuO) ₂	CL 77 (1986)
p-Ph ₂ SiHC ₆ H ₄ SiHPh ₂ , (t-BuO) ₂	CL 119 (1988)



R = 1°, 2° alkyl

CC 1588 (1985)
JACS 109 7534 (1987)
Chem Pharm Bull 35 3967 (1987)
TL 29 2727 (1988); 32 6003 (1991)
Nucleosides and Nucleotides 8 743 (1989)



cat Pd(OAc)₂-n-Bu₃P JOC 57 1326 (1992)
SL 291 (1993)

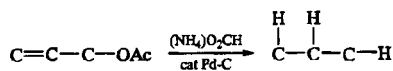
cat Pd(acac)₂-n-Bu₃P JOC 57 1326 (1992)
SL 113 (1993)



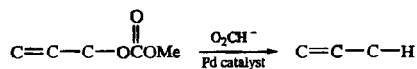
Li, NH₃ JOC 57 3173 (1991)
NaBH₄, cat Pd(PPh₃)₄ TL 33 2921 (1992)
JACS 117 11106 (1995)
(NH₄)O₂CH, cat Pd₂(DBA)₃·CHCl₃ CL 1017 (1984)
JACS 117 11106 (1995)
(NH₄)O₂CH, cat Pd₂(DBA)₃·CHCl₃-n-Bu₃P CL 1017 (1984)
(NH₄)O₂CH, cat PdCl₂(PPh₃)₂ TL 613 (1979)
JOC 60 4339 (1995)

NaO_2CH , cat $\text{Pd}(\text{OAc})_2$, cat PPh_3 , cat 15-crown-5	SL 949 (1994)
Ph_2SiH_2 , cat $\text{Pd}(\text{PPh}_3)_4$	Israel J Chem 24 82 (1984)
$\text{Me}_3\text{SiO}(\text{OSiHMe})_{40}\text{SiMe}_3$, cat $\text{Pd}(\text{PPh}_3)_4$	Israel J Chem 24 82 (1984)
Ph_2SiH_2 , ZnCl_2 , cat $\text{Pd}(o\text{-Tol}_3\text{P})_4$	JOC 53 3723 (1988)
$n\text{-BuZnCl}$, cat $\text{Pd}(\text{OAc})_2$, cat PPh_3	SL 949 (1994)
$\text{Zn}(\text{Hg})$, HCl	TL 725 (1972) Org Syn Coll Vol 6 769 (1988)
SmI_2 , THF, HMPA, $\text{Me}_3\text{CCO}_2\text{H}$	TL 29 6947 (1988)
SmI_2 , cat $\text{Pd}(\text{PPh}_3)_4$, $i\text{-PrOH}$	TL 27 601 (1986)

See page 229, Section 4, for reduction of allylic esters with double bond transposition.



JOC 59 4714 (1994)



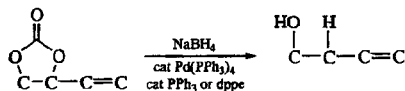
CL 1017 (1984)

TL 33 2987 (1992)

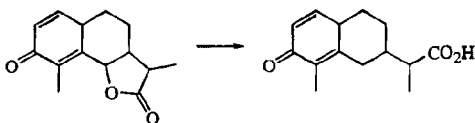
JOC 57 6090 (1992); 59 5847 (1994)

JACS 116 775 (1994)

See also page 229, Section 4.



TL 32 6081 (1991)

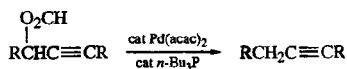


Zn, HOAc, ultrasound

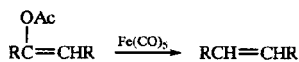
TL 36 8469 (1995)

PhSH or PhSeH, NaH

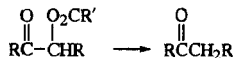
TL 32 3413 (1991)



TL 34 2161 (1993)



TL 447 (1973)

Ca, NH₃

JCS 4344 (1956)

Zn, HOAc

JACS 77 4367 (1955); 79 5540 (1957)

JOC 57 7175 (1992)

Zn(Hg), HOAc

JACS 97 1101 (1975)

CrCl₂

TL 2553 (1978)

JOC 55 1589 (1990)

Fe(CO)₅

TL 447 (1973)

SmI₂, THF

TL 35 1665 (1994)

SmI₂, ROH

JOC 51 1135 (1986)

JACS 115 3816 (1993)

TL 35 1477 (1994); 36 1661 (1995)

SmI₂, HOAc

JOC 59 4015 (1994)

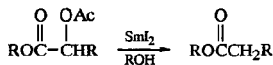
n-Bu₃SnH

Ber 110 2911 (1977)

CC 1290 (1987)

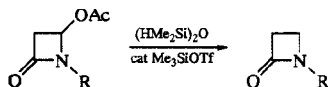
n-Bu₄NF·*n*H₂O, HS(CH₂)₃SH,
N-methylmorpholine

TL 36 7467 (1995)

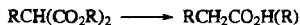


TL 30 2945 (1989); 32 573 (1992)

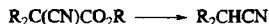
SL 863 (1994)



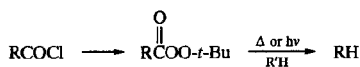
CC 1743 (1987)



See page 1724, Section 2.



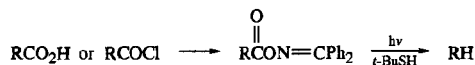
See page 1716, Section 2.



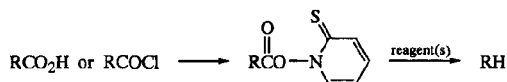
JACS 83 3998 (1961); 86 3157 (1964); 102 678 (1980)

JOC 33 99 (1968); 59 6490 (1994)

Ber 108 2156 (1975)



TL 28 6207 (1987)

Reagent(s)*n*-Bu₃SnH

CC 939 (1983)

Heterocycles 21 1 (1984)

Tetr 41 3901 (1985)

TL 34 5751 (1993)

JOC 59 5543 (1994)

t-BuSH, *hν*

CC 939 (1983); 1298 (1984); 1041 (1987)

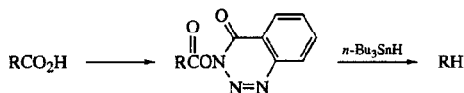
JACS 112 8971 (1990)

TL 31 1897 (1990)

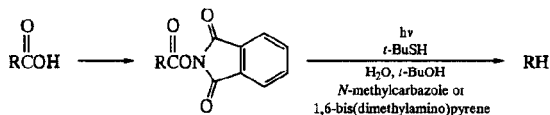
SL 395 (1993)

t-BuSH

SL 38 (1990)



TL 30 2341 (1989)



JACS 110 8736 (1988)

JOC 56 5826 (1991)



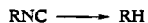
Helv 63 1562, 2328 (1980)

JACS 107 3285 (1985)

JOC 56 1393 (1991)

17. Nitriles

	$\text{RCN} \longrightarrow \text{RCH}_3$	
H_2 , cat $\text{Ni-Al}_2\text{O}_3$		Syn 802 (1980)
H_2 , cat Pd-C		Ann 707 26 (1967)
$(\text{NH}_4)_2\text{O}_2\text{CH}$, cat Pd-C		Syn 1036 (1982)
	$\text{RCN} \longrightarrow \text{RH}$	
electrolysis, EtNH_2		TL 1975 (1968)
Li , NH_3 , EtOH		TL 28 547 (1987); 29 631, 1391 (1988) (all α -amino nitriles)
Li , EtNH_2		JACS 89 6794 (1967); 91 2059 (1969)
Li naphthalenide		TL 27 2199 (1986)
Li , Na or K ; HMPA ; (<i>t</i> - BuOH)		Compt Rend 274 797 (1972) BSCF 1174 (1973) TL 3851 (1975) Syn 391 (1976)
Na , NH_3		JACS 89 6794 (1967); 91 2059 (1969) BSCF 178 (1975) JOC 40 1162 (1975); 42 3309 (1977); 55 5550 (1990) (α -alkoxy nitrile) TL 57 (1976); 61 (1976) (α -amino nitrile); 27 (1979); 23 3369 (1982) (α -amino nitrile) Chem Pharm Bull 25 2689 (1977) (α -amino nitrile)
Na , $\text{Fe}(\text{acac})_3$		JACS 93 7113 (1971)
K , crown ether, toluene		TL 26 6103 (1985) JOC 57 2732 (1992)
K , <i>t</i> - BuOH , HMPA , Et_2O , toluene		JACS 115 11485 (1993)
K , Al_2O_3		JOC 45 3227 (1980)
NaOH		Syn 290 (1979) (<i>o</i> -hydroxyaryl nitrile)
KOH		Syn Commun 10 939 (1980)
BH_3		JOC 56 2920 (1991) (α -amino nitrile)
NaBH_4		TL 3105 (1969) (α -amino nitrile); 23 3369 (1982) (α -amino nitrile)
NaBH_3CN		TL 29 6831 (1988) (α -amino nitrile)
$\text{Zn}(\text{BH}_4)_2$, AgOTf		TL 36 2991 (1995) (α -amino nitrile)
RLi		JOC 55 1479 (1990) ($\text{R} = 3^\circ$ benzylic)
	$\text{RCHXCN} \longrightarrow \text{RCH}_2\text{X}$	
<u>X</u>	<u>Reagent</u>	
CO_2R , CN	SmI_2	TL 36 7661 (1995)
CN	<i>n</i> - Bu_3SnH	JACS 112 9401 (1990) SL 107 (1991) TL 36 5159 (1995)

18. Isonitriles

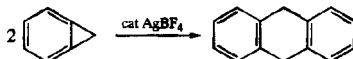
K, toluene, crown ether/ <i>i</i> -PrOH	TL 30 845 (1989)
(Me ₃ Si) ₂ SiHMe	JOC 57 3405 (1992)
(Me ₃ Si) ₃ SiH	JOC 58 1646 (1993)
(RS) ₃ SiH	SL 219 (1990)
	JOC 57 2427 (1992)
<i>n</i> -Bu ₃ SnH	JACS 90 4182 (1968)
	JCS Perkin I 2657 (1980)
polymer-Sn(<i>n</i> -Bu) ₂ H	JOC 56 5971 (1991)
(Et ₃ NH)H ₂ PO ₂	JOC 58 6838 (1993)

2. COUPLING REACTIONS

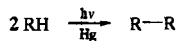
See also page 67, Section 12.7.

1. Symmetrical or Intramolecular Coupling

See also page 168, Section 3; page 175, Section 5; and page 185, Section 7.



TL 35 4493 (1994)

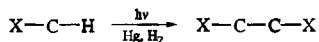


CC 970 (1987)

TL 28 5599 (1987)

JACS 111 2935 (1989); 113 2233 (1991)

SL 597 (1991) (review)



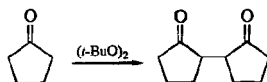
X = COR, CO₂H, CO₂R, OH, O₂CR, NR₂, NRCOR, CN

TL 30 5583 (1989)

JACS 113 2233 (1991)

SL 597 (1991) (review)

JOC 58 3895 (1993)

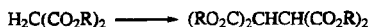


JOC 53 5383 (1988)



X, Y = COR, COR; COR, CO₂R; CO₂R, CO₂R; CO₂R, CN

TL 36 8757 (1995)



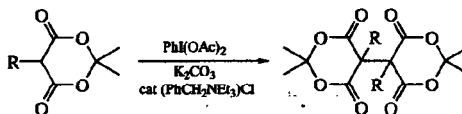
H₂, Hg, hv JACS 113 2233 (1991)

NaI, electrolysis Org Syn Coll Vol 7 482 (1990)

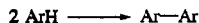
KI, electrolysis BCSJ 37 1794 (1964)

NaOEt/electrolysis JCS C 1352 (1967); 1153 (1970)

NaOEt/Br₂ JACS 78 2287 (1956)



JOC 56 459 (1991)



Reviews:

Angew Int 2 723 (1963)

W. I. Taylor, A. I. Battersby, "Oxidative Coupling of Phenols," M. Dekker, New York (1967)

Russ Chem Rev 47 649 (1978)

Tetr 36 3327 (1980)

Chem Rev 87 357 (1987)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 2.9, pp 659-701

electrolysis

TL 32 7593 (1991)

CL 81 (1993)

DDQ (ArOH)

JOC 59 3701 (1994)

Pb(OAc)₄, BF₃·OEt₂

JACS 102 6504 (1980)

TeCl₄/Raney Ni

Org Syn Coll Vol 6 468 (1988)

PhI(OAc)₂, CF₃CO₂H

JOC 50 743 (1985); 52 5662 (1987); 53 2318 (1988)
(all intramolecular)

(Et₄N)[I(O₂CCX₃)₂] (X = H, F, Cl)

TL 21 3509 (1980)

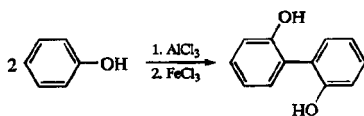
VOF₃, CF₃CO₂H, [(CF₃CO)₂O]

JACS 95 6861 (1973); 97 5622, 5623 (1975); 98 267
(1976) (all intramolecular)

JOC 41 3772, 4047 (1976); 43 2521, 4076 (1978); 52
5662 (1987) (all intramolecular)

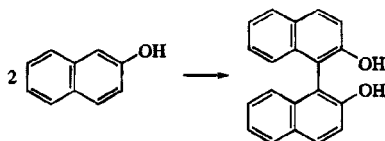
TL 27 1785 (1986); 36 5895 (1995) (both
intramolecular)

$\text{VOF}_3, \text{BF}_3 \cdot \text{OEt}_2$	JOC 59 635 (1994) (intramolecular)
$\text{VOF}_3, \text{BF}_3 \cdot \text{OEt}_2, \text{AgBF}_4$	SL 43 (1995) (intramolecular)
VOCl_3	JOC 50 743 (1985); 52 5662 (1987); 53 2318 (1985) (all intramolecular) TL 27 1785 (1986) (intramolecular)
$\text{VOCl}_3, \text{CF}_3\text{CO}_2\text{H}, (\text{CF}_3\text{CO})_2\text{O}$	Tetr 47 3787 (1991)
$\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O} (\text{ArOH})$	JOC 59 3701 (1994)
$\text{FeCl}_3 \cdot 6\text{H}_2\text{O} (\text{ArOH})$	JOC 54 3007 (1989); 59 3701 (1994) Tetr 48 9483 (1992)
$\text{FeCl}_3, \text{SiO}_2 (\text{ArOH}, \text{ArOR})$	JOC 45 749 (1980); 46 4545 (1981)
$\text{FeCl}_3, \text{Ac}_2\text{O}$	Chem Pharm Bull 33 3599 (1985)
$\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}, \text{CH}_3\text{CN}$	Chem Pharm Bull 33 3599 (1985)
$\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}, \text{CF}_3\text{CO}_2\text{H}$	TL 33 4161, 4165 (1992); 35 3733 (1994) JOC 58 5717 (1993); 60 4339 (1995) SL 605 (1994) (all intramolecular)
$\text{K}_3\text{Fe}(\text{CN})_6 (\text{ArOH})$	JOC 46 2547 (1981)
$\text{RuO}_2, \text{BF}_3 \cdot \text{OEt}_2, \text{CF}_3\text{CO}_2\text{H}, (\text{CF}_3\text{CO})_2\text{O}$	TL 27 1785, 5377 (1986); 28 543, 5161 (1987) JOC 53 224 (1988) Tetr 47 3787 (1991) (all intramolecular)
$\text{RuO}_2, \text{BF}_3 \cdot \text{OEt}_2, \text{CF}_3\text{SO}_3\text{H}, (\text{CF}_3\text{SO}_2)_2\text{O}$	JOC 53 224 (1988) (intramolecular) Tetr 47 3787 (1991)
$\text{CoF}_3, \text{CF}_3\text{CO}_2\text{H}$	JACS 102 6504 (1980)
$\text{Pd}(\text{OAc})_2$ (pyrroles)	CC 49 (1980)
CuCl_2 , amine (ArOH)	JOC 58 4534 (1993)
air, cat $\text{CuCl}(\text{OH}) \cdot \text{TMEDA} (\text{ArOH})$	TL 35 7983 (1994)
$\text{Ti}(\text{O}_2\text{CCF}_3)_3$	JACS 107 4984 (1985) JOC 52 5662 (1987); 53 2318 (1985) (all intramolecular)
$\text{Ti}(\text{O}_2\text{CCF}_3)_3, \text{BF}_3 \cdot \text{OEt}_2$	JOC 42 764 (1977) (also intermolecular); 49 3220 (1984); 53 224 (1988) CC 538 (1977) JACS 102 6504, 6513 (1980) Syn Commun 10 827 (1980) Austral J Chem 37 1775 (1984) TL 27 1465, 1781, 1785 (1986); 28 543, 5161 (1987); 29 4839 (1988) Tetr 47 3787 (1991) (all intramolecular)
$\text{Ti}(\text{O}_2\text{CCF}_3)_3$, cat $\text{Pd}(\text{OAc})_2$	TL 22 3793 (1981)



Tetr 48 9483 (1992)

TL 33 2207 (1992)



electrolysis

CL 81 (1993)

DDQ

JOC 59 3701 (1994)

 VCl_4

JOC 34 2388 (1969)

 VOCl_3

JOC 34 2388 (1969)

 $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$

JOC 59 3701 (1994)

 $\text{Mn}(\text{acac})_3$

JACS 90 7134 (1968)

CC 1111 (1984)

Angew Int 27 1705 (1988)

Israel J Chem 29 201 (1989)

 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

Ber 59 2159 (1926)

JOC 46 4988 (1981); 54 3007 (1989); 59 3701 (1994)

 $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, microwave irradiation

SL 435 (1994)

 $\text{K}_3\text{Fe}(\text{CN})_6$

JOC 46 2547 (1981)

air, cat $\text{CuSO}_4 \cdot \text{Al}_2\text{O}_3$

JOC 59 6859 (1994)

 $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, *t*-BuNH₂

Org Prep Proc Int 23 200 (1991)

JOC 59 3151 (1994)

 $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, sparteine (enantioselective)

JOC 57 1917 (1992); 58 4534 (1993)

 $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{PhCH}(\text{NH}_2)\text{CH}_3$ (enantioselective)

JOC 58 4534 (1993)

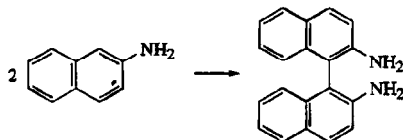
 $\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, various RNH₂ (enantioselective)

Tetr 41 3313 (1985)

 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{PhCH}(\text{NH}_2)\text{R}$ (enantioselective)

Bioorg Chem 7 397 (1978)

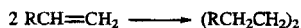
CC 1490 (1984)



$\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, *t*-BuNH₂ JOC 59 2156 (1994)

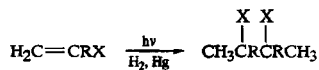
$\text{CuCl}_2 \cdot 4\text{H}_2\text{O}$, sparteine (enantioselective) JOC 57 1917 (1992)

$(\text{PhCH}_2\text{NH}_2)_4\text{CuCl}_2$ SL 231 (1991)



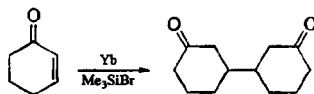
$\text{BH}_3 / \text{AgNO}_3$, NaOH JACS 83 1001, 1002 (1961)

LiAlH_4 , TiCl_4 or $\text{Cp}_2\text{TiCl}_2 / \text{Cu}(\text{OAc})_2$ CL 1155, 1337 (1978)

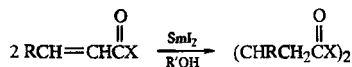


X = alkyl, CO₂R, CN, OAc

TL 30 3389 (1989)



TL 35 4111 (1994)

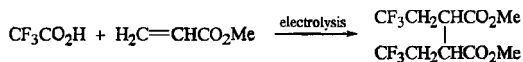


X = OR, NR₂

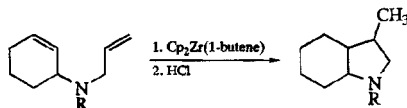
TL 32 6557 (1991)



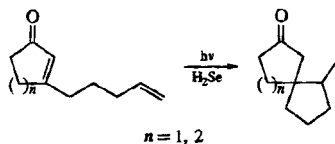
Org Syn Coll Vol 7 479 (1990)



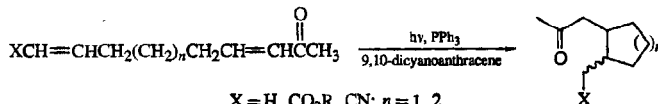
JOC 54 872 (1989)



JOC 57 3519 (1992)



JACS 117 5339 (1995)



TL 35 7837 (1994)



Review: Tetr 36 3327 (1980)

Li, ultrasound

TL 22 2757 (1981); 30 3567 (1989) (Ar = pyridine);
32 7133 (1991)*t*-BuLi / CuCN / O₂

TL 35 815 (1994)

Cu (Ullman)

Chem Rev 38 139 (1946); 64 613 (1964) (reviews)

Syn 9 (1974) (review)

Ann 329 (1977)

JOC 44 3445 (1979); 50 5092 (1985); 56 3192

(1990); 59 2577, 2655 (1994); 60 6427 (1995)

BCSJ 54 3522 (1981)

JACS 106 3297 (1984); 114 9309 (1992)

TL 32 6919 (1991) (intramolecular); 33 5103 (1992)

(intramolecular); 34 3061 (1993); 35 3259 (1994);

36 5869, 5921 (1995)

Co

JOC 48 4904 (1983)

Ni

TL 23 4215 (1982)

JOC 48 840, 4904 (1983)

Ni(COD)₂

JACS 93 5908 (1971); 103 6460 (1981)

Ni(COD)₂, hv, *N*-methylimidazole
(X = Br, I, OTf)

JOC 58 997 (1993)

Ni(PPh₃)₄

JACS 97 3873 (1975); 103 6460 (1981)

TL 3375 (1975); 21 631 (1980)

JOC 52 4665 (1987) (intramolecular)

Ni(ClO₄)₂, electrolysis

JCS Dalton 1074 (1981)

Ni(acac)₃, electrolysis

JOC 41 719 (1976)

NiCl₂(PPh₃)₂, electrolysis

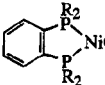
JOMC 202 435 (1980)

J Chem Res (S) 26 (1980)

NiCl₂(PPh₃)₂, Zn, PPh₃

SL 525 (1990)


TL 4089 (1977)

$\text{NiCl}_2(\text{dppe})$, electrolysis	Organomet 7 2203 (1988)
 NiCl_2 ($\text{R} = i\text{-Pr}$), electrolysis	JOC 56 3246 (1991)
NiBr_2 , KI, Zn, HMPA	BCSJ 53 3691 (1980)
LiH , $t\text{-BuOH}$, $\text{Ni}(\text{OAc})_2$, PPh_3 or bipy	TL 36 6051 (1995)
NaH , $\text{NaO}-i\text{-Am}$, $\text{Ni}(\text{OAc})_2$, bipy	TL 3951 (1977)
NaH , $\text{NaO}-i\text{-Bu}$, $\text{Ni}(\text{OAc})_2$, PPh_3	TL 27 5483 (1986) (heteroaromatic)
NaH , $t\text{-AmOH}$, $\text{Ni}(\text{OAc})_2$, PPh_3 or bipy	JOMC 264 263 (1984)
NaH , $t\text{-AmOH}$, $\text{Ni}(\text{OAc})_2$, bipy, KI	JOC 54 4840 (1989)
cat $\text{Pd}(\text{Hg})$, N_2H_4	BCSJ 53 1767 (1980)
cat $\text{Pd}-\text{C}$, NaOH , NaO_2CH , surfactant	Syn 537 (1978) JOC 47 4116 (1982) (bipyridines)
cat $\text{Pd}(\text{OAc})_2$, R_3N	JCS Perkin I 121 (1975) SL 809 (1991)
cat $\text{Pd}(\text{OAc})_2$, $n\text{-Bu}_3\text{N}$, cat Ph_3As	SL 809 (1991)
cat $\text{Pd}(\text{OAc})_2$, cat PPh_3 , $(\text{Me}_3\text{Sn})_2$	TL 32 3859 (1991) (intramolecular)
cat $\text{Pd}(\text{PPh}_3)_4$, 0.5 $(\text{Me}_3\text{Sn})_2$, LiCl	JACS 109 5478 (1987)
cat $\text{Pd}(\text{PPh}_3)_4$, $(\text{R}_3\text{Sn})_2$ ($\text{R} = \text{Me}$, $n\text{-Bu}$) ($\text{X} = \text{Br}$, I , OTf)	TL 31 161 (1990) (intramolecular)
cat $\text{Pd}(\text{PPh}_3)_4$, electrolysis	TL 26 1655 (1985)
Zn, NiCl_2 , PPh_3	Syn 736 (1984) (bipyridines)
Zn, NiCl_2 , PPh_3 , KI	TL 35 8985 (1994)
Zn, cat $\text{NiCl}_2(\text{PPh}_3)_2$, cat PPh_3	TL 4089 (1977)
Zn, $\text{NiCl}_2(\text{PPh}_3)_2$, $n\text{-Bu}_4\text{NI}$	CC 1476 (1987) (bithiophenes)
Zn, cat $\text{NiCl}_2(\text{PEt}_3)_2$, KI	BCSJ 57 1887 (1984)
Zn, NiBr_2 , KI	CL 917 (1979) BCSJ 53 3691 (1980)
Zn, $\text{NiBr}_2(\text{PPh}_3)_2$, $n\text{-Bu}_4\text{NI}$	TL 26 3829 (1985)
Zn, Mg or Mn; cat NiCl_2 , PPh_3	JOC 51 2627 (1986) TL 35 3957 (1994)



For $\text{R} =$ allylic and vinylic, see also page 463, Section 7.

Li, ultrasound ($\text{R} = 1^\circ$ alkyl, benzyl)	TL 22 2757 (1981)
Na (Wurtz) ($\text{R} =$ alkyl)	JACS 80 622 (1958)

Na-K (R = 3° alkyl)	JOC 57 5484 (1992)
Mg graphite (R = 1° alkyl)	JOC 54 2307 (1989)
Al, cat Cp_2TiCl_2 (R = benzylic, allylic)	SL 489 (1991)
O_2 , Et_3B (R = allylic, benzylic)	JACS 93 1508 (1971)
$(n\text{-Bu}_3\text{Sn})_2$, $h\nu$ (RX = $\text{PhCHBrCO}_2\text{R}$)	SL 286 (1993)
Ti, V (review; R = allylic, benzylic)	Org Prep Proc Int 12 361 (1980)
TiCl_3 or TiCl_4 , LiAlH_4 (R = allylic, benzylic)	Syn 607 (1976)
$\text{VCl}_2(\text{py})_4$ (R = benzylic)	JACS 95 4158 (1973)
VCl_3 , LiAlH_4 (R = allylic, benzylic)	Syn 170 (1977)
CrCl_2 (R = benzylic)	Tetr 20 1005 (1964)
CrCl_2 , electrolysis (R = allylic, benzylic)	Syn 901 (1978)
CrCl_3 , LiHBEt_3 (R = 3° alkyl, allylic, benzylic)	TL 22 5167 (1981)
CrCl_3 , LiAlH_4 (R = allylic, benzylic)	TL 3829 (1977) BCSJ 55 561 (1982)
$\text{Li}[\text{CpFe}(\text{COD})](\text{TMEDA})$ (R = allylic, benzylic)	JACS 116 2889 (1994)
$\text{Fe}_3(\text{CO})_{12}$, pyridine <i>N</i> -oxide (R = allylic, benzylic)	CL 1309 (1978)
$\text{Fe}(\text{acac})_3$, electrolysis (R = 1° alkyl)	JOC 41 719 (1976)
$\text{CoCl}(\text{PPh}_3)_2$ (R = benzylic)	CL 1277 (1981)
Ni (R = benzylic)	TL 23 4215 (1982) JOC 48 4904 (1983)
$\text{Ni}(\text{CO})_4$, DMF (R = allylic)	JACS 73 2654 (1951); 86 1641 (1964); 89 2757, 2758 (1967); 90 2416, 2417 (1968); 96 4724 (1974) TL 6237 (1966) Org Rxs 19 115 (1972) (review)
$\text{Ni}(\text{PPh}_3)_4$ (R = allylic, vinylic)	TL 3375 (1975) JACS 103 6460 (1981)
$\text{NiBr}_2(\text{PPh}_3)_2$, Zn, Et_4NI (R = benzylic)	CL 127 (1985) TL 26 4777 (1985) (intramolecular)
$\text{NiBr}_2(\text{PPh}_3)_2$, Zn, Et_4NI (RX = ArCOCH_2Cl)	TL 26 3719 (1985)
$\text{Ni}(\text{acac})_2$, electrolysis (R = benzylic)	JOC 41 719 (1976)
$\text{Ni}(\text{ClO}_4)_2$, electrolysis (R = 1°, 3° alkyl; benzylic)	JCS Dalton 1074 (1981)
cat $\text{Pd}(\text{OAc})_2$, cat PPh_3 , $(\text{Me}_3\text{Sn})_2$ (R = benzylic)	TL 32 3859 (1991) (intramolecular)
cat PdCl_2 , NaOH, N_2H_4 (R = 1° alkyl)	BCSJ 54 3599 (1981)
 NLi, CuI (R = allylic)	TL 783 (1979)

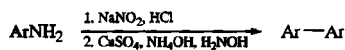
$\text{CuI} \cdot \text{PR}'_3$ ($\text{R}' = \text{Et}, n\text{-Bu}$), $\text{LiC}_{10}\text{H}_8$
($\text{R} = 1^\circ > 2^\circ > 3^\circ$ alkyl, allylic, benzylic)

JOC 55 584 (1990)

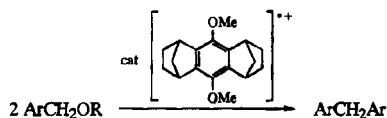
$\text{CuI}, \text{K}, \text{C}_{10}\text{H}_8$ ($\text{R} = \text{allylic}$)

JOC 44 3445 (1979)

	$\text{RX} \longrightarrow \text{RM} \xrightarrow{\text{reagent(s)}} \text{R}-\text{R}$	
<u>RM</u>	<u>Reagent(s)</u>	
ArCH_2Li	CoCl_2	BSCF 1331 (1964)
ArLi	$\text{Fe}(\text{acac})_3$	JACS 106 2160, 3286 (1984); 109 7068 (1987); 114 10775 (1992)
		JOC 60 6813 (1995)
	FeCl_3	TL 32 859 (1991)
	CoCl_2	BSCF 1331 (1964)
		JACS 101 3553 (1979)
	$\text{NiBr}_2(\text{PPh}_3)_2$	TL 34 3413 (1993)
	CuCl_2	CC 1476 (1987) (bithiophenes)
		JACS 115 8716 (1993) (poly- thiophenes); 117 2467 (1995) (bithiophenes)
	CuCN/O_2	TL 35 5567 (1994) (intra- molecular)
	$\text{CuCN} \cdot \text{TMEDA}/\text{O}_2$	JACS 116 8795 (1994)
RMgX ($\text{R} = 1^\circ$ alkyl)	Ag	TL 34 4297 (1993)
	AgOTf	JOC 41 2882 (1976) (cyclo- butanes and -pentanes)
	RX, Ag or AgX	Syn 303 (1971)
RMgX ($\text{R} = 2^\circ$ alkyl, aryl)	TiBr	JACS 90 2423 (1968)
		Tetr 26 4041 (1970)
		JOC 51 1618 (1986)
		Org Syn Coll Vol 6 488 (1988)
RMgX ($\text{R} = 1^\circ$ alkyl, benzylic, aryl)	CoCl_2	BSCF 1331 (1964)
RMgX ($\text{R} = 1^\circ$ alkyl, benzyl, vinyl, phenyl)	CuCl	Angew Int 6 85 (1967)
	AgBr	BCSJ 44 3063 (1971)
		BCSJ 44 3063 (1971)
ArMgX	$\text{Ni}(\text{acac})_2$ or NiCl_2L_2	JOC 41 2252 (1976)
	$\text{NiCl}_2(\text{PPh}_3)_2$	TL 29 6199 (1988)
	$\text{H}_2\text{C}=\text{C}(\text{Cl})\text{CH}_2\text{Cl}$	TL 29 1293 (1988)
	$\text{ClCH}_2\text{CH}=\text{CHCH}_2\text{Cl}$ or $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Cl}$	JOC 46 2194 (1981)
RCu or R_2CuLi ($\text{R} = 1^\circ, 2^\circ$ alkyl; aryl; vinylic; alkynyl)	$\Delta, \text{O}_2, \text{PhNO}_2$ or $\text{CuCl}_2 \cdot \text{TMEDA}$	JACS 88 4541 (1966); 89 5302 (1967); 93 1379 (1971)
		Angew Int 13 291 (1974)
		JOC 44 2705 (1979)
$(\text{ArCu})_n$	CuOTf	CC 203 (1977)



JACS 114 6227 (1992)



JOC 60 7479 (1995)



R = allylic, benzylic

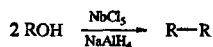
JACS 87 3277 (1965); 90 209, 3284 (1968)

CC 53 (1969)

JOC 40 2687 (1975); 43 3249 (1978)

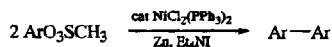
J Med Chem 23 841 (1980)

Org Prep Proc Int 12 361 (1980) (review)

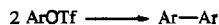


R = allylic, benzylic

CL 157 (1982)



JOC 60 176, 1066 (1995)



CL 407 (1986)

Zn, cat NiCl₂, PPh₃, NaI

Macromolecules 25 1816 (1992) (polymer)

Zn, cat NiCl₂, cat bipy, PPh₃

SL 568 (1993)

Zn, cat NiCl₂(dppe), KI

SL 568 (1993)

Zn, cat PdCl₂(PPh₃)₂

TL 31 161 (1990)

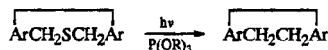
(Me₃Sn)₂, cat Pd(PPh₃)₄

JACS 115 5843 (1993)

(both intramolecular)

electrolysis, cat PdCl₂(PPh₃)₂

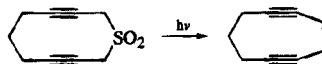
CC 1729 (1992)



TL 1215 (1973)

Syn Commun 6 591 (1976)

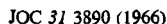
CL 977 (1977)


$$\text{ArCH}_2\text{SO}_2(\text{CH}_2)_n\text{SO}_2\text{CH}_2\text{Ar} \xrightarrow{\Delta} \text{Ar}(\text{CH}_2)_{n+2}\text{Ar}$$
$$\text{Ar} \begin{array}{c} \text{NO} \\ | \\ \text{CH}_2\text{NCH}_2\text{Ar} \end{array} \xrightarrow[\text{KOH}]{\text{Na}_2\text{S}_2\text{O}_4} \text{ArCH}_2\text{CH}_2\text{Ar}$$
$$\text{RM} \longrightarrow \text{R}-\text{R}$$
Reagent

Organomet 1 542 (1982)

JOC 42 1680 (1977)

BCSJ 50 2741 (1977)



"Organic Electrochemistry," Ed. M. M. Baizer, M. Dekker, New York (1973), p 469

"Techniques of Chemistry." Ed. N. L. Weinberg, J. Wiley, New York (1974), Vol 5, Part 1, p 793

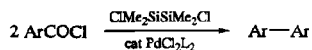
Org Syn 60 1 (1981)

Can J Chem 59 945 (1981)

Angew Int 20 911 (1981)

Org Syn Coll Vol 7 181 (1990)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 2.8, p 633

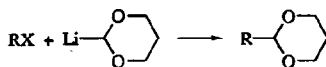


JOC 55 5430 (1990)

2. Unsymmetrical Coupling

2.1. Organolithium Reagents

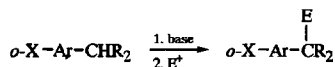
See also page 67, Section 12.7.



JACS 111 1381 (1984)




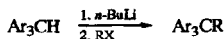
<u>Ar</u>	<u>E⁺</u>	
benzene	MeI	TL 32 1483 (1991)
	RX	TL 32 3369 (1991)
	R ₂ SO ₄ (R = Me, Et)	JOC 47 3949 (1982)
	R ₂ CO	TL 36 8221 (1995)
	CO ₂	TL 32 3369 (1991)
phenol	RX, CO ₂ , R ₃ MCl (M = Si, Sn)	JOC 51 1432 (1986)
naphthalene	MeI, Me ₃ SiCl	JOC 44 3483 (1979); 48 903 (1983)
pyridine	RBr	TL 24 31 (1983)
pyrazine	RCHO	JOC 52 3971 (1987)
oxazole	MeOD, RX, RCHO, R ₂ CO	TL 24 4391 (1983); 28 3585 (1987)
		JACS 107 1423 (1985)
thiazole	RX	TL 28 3585 (1987)
binaphthyl	MeSi(OMe) ₃	TL 29 6199 (1988)



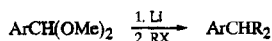
Review: Org Rxs 47 1 (1995)

X	E^+	
OMe	RX	JOC 56 1696 (1991)
NHCOCMe ₃	—	JOC 54 509 (1989)
NHCO ₂ Li	RX, RCHO, R ₂ CO	JOC 56 5045 (1991)
CH ₂ OH	D ₂ O, RX, RCHO, R ₂ CO, CO ₂	TL 24 1233 (1983)
	Me ₃ SiCl	JACS 109 2738 (1987)
	<i>n</i> -Bu ₃ SnCl	JACS 110 2014 (1988)
CH=NR	RX	JOC 58 2463 (1993); 59 2616 (1994)
Cl	CO ₂	JOC 58 2463 (1993)
	HCONMe ₂ , RCON(Me)OMe	JOC 58 2631 (1993)
CO ₂ H	RX, R ₂ CO	JACS 92 1396 (1970) (also <i>m</i> and <i>p</i> isomers)
Br	RCHO	JACS 104 4708 (1982)
	(RO) ₂ CO	CC 479 (1986)
		JACS 99 4533 (1977)
		Syn 245 (1977)
		JOC 42 4155 (1977)
CO ₂ R	RX	JCS Perkin I 1043 (1984)
		JACS 108 4953 (1986)
	RCHO, R ₂ CO	CC 764 (1983), 520 (1987)
		JCS Perkin I 1043 (1984)
		TL 30 2509 (1989)
		(Ar = indole)
	RCOCl, CO ₂	JCS Perkin I 1043 (1984)
	other electrophiles	CC 406 (1978); 205, 206 (1979)
		JCS Perkin I 1043 (1984)
CONHR	RCHO, R ₂ CO	JOC 29 3514 (1964); 52 5378 (1987)
		J Heterocyclic Chem 6 83 (1969)
	ArCH=NR	JOC 52 5378 (1987)
	RCO ₂ R	JACS 111 4522 (1989)
	HCONMe ₂ , RCON(Me)OMe	JOC 57 2700 (1992)
	RCN	JOC 47 3787 (1982)
CONR ₂	RX	JOC 55 1375 (1990)
	RX, sparteine	JACS 116 9755 (1994) (chiral)
	RX, ArX	JACS 113 4931 (1991)
	RX, R ₂ CO	JOC 38 1668 (1973) (also <i>m</i> and <i>p</i> isomers)
	ArCH=NR	JOC 52 5378 (1987)
	RCO ₂ R	JOC 54 4715 (1989)
	lactone	TL 36 3003 (1995)
	anhydride	JOC 58 7158 (1993)
	RCN	JACS 108 7100 (1986); 110 6471 (1988)

<u>X</u>	<u>E⁺</u>	
CONR ₂ (continued)	O ₂ Me ₃ SiCl	JOC 52 674 (1987) JOC 51 3325 (1986); 54 4372, 4386 (1989)
CONEtCH ₂ CH ₂ NEt ₂	RX, RCHO, HCONMe ₂	JOC 51 3566 (1986)
	RX	CC 388 (1986)



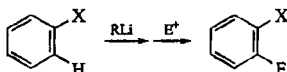
Ber 119 2647 (1986)
JOC 58 3748 (1993)



TL 35 6759 (1994)



JOC 58 6526 (1993)
TL 35 5189 (1994)



E⁺ = RX, RCHO, R₂CO, CO₂, DMF, RCO₂R, (RCO)₂O, (RS)₂, ClSiMe₃, I₂, TsN₃

Reviews and key references:

- Org Rxs 8 258 (1954); 26 1 (1979)
Chem Rev 69 693 (1969); 90 879 (1990)
TL 3443 (1970)
Adv Chem Ser 130 222 (1974)
JOC 41 3653 (1976)
Z Chem 17 1 (1977)
Tetr 39 2009 (1983) (π-deficient heteroaromatics)
Syn 957 (1983) (synthesis of heterocycles)
Pure Appl Chem 62 671, 2047 (1991); 66 2155 (1994)
Adv Heterocyclic Chem 52 189 (1991) (heterocycles)
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 3, Part 1.6, p 241

X
C≡CH

CC 366 (1981)
TL 22 2495 (1981)
JOC 55 1311 (1990)
SL 853 (1993)

- F** JOC 22 1915 (1957); 46 203 (pyridines), 4494 (pyridines) (1981); 50 805 (1985); 52 713 (1987); 53 3145 (1988); 55 773 (1990)
J Med Chem 11 814 (1968); 29 1982 (1986)
Compt Rend C 275 1535 (1972) (pyridines)
JOMC 171 273 (1979) (quinolines); 215 139 (1981) (pyridines)
Tetr 39 2009 (1983) (heteroaromatics)
TL 28 4139 (1987); 33 7495, 7499 (1992); 35 389 (1994); 36 659, 881 (1995)
SL 747 (1990); 731 (1991); 360 (1992)
- Cl** TL 21 4137 (1980) (pyridines); 36 881 (1995)
JOMC 216 139 (1981) (pyridines)
JOC 55 3622, 4971 (1990)
- Br** TL 21 4137 (1980) (pyridines); 24 3291 (1983) (pyridines)
Tetr 38 3035 (1982) (pyridines)
J Chem Res (S) 278 (1982) (pyridines)
- I** TL 21 4137 (1980) (pyridines)
- CF₃** JACS 68 1658 (1946)
JOMC 11 209 (1968)
SL 747 (1990)
- OH** JOC 19 510 (1954); 53 4263, 5345 (naphthols) (1988)
Chem Rev 57 583 (1957) (review)
J Chem Eng Data 14 388 (1969)
Org Prep Proc Int 13 426 (1981)
JACS 107 2571 (1985); 112 1467 (1990) (theory, naphthols)
- OMe** JACS 62 667, 987 (1940); 80 4537 (1958); 106 7150 (1984); 107 2712 (1985); 109 7068 (1987); 111 665, 7191 (1989); 113 6865 (1991); 115 5859 (1993); 116 10815 (1994)
Ber 73 1197 (1940); 112 1841 (1979)
JOMC 9 193 (1967); 11 209, 217 (1968); 132 321 (1977); 182 155 (1979)
Tetr 25 3509 (1969)
TL 3443 (1970); 27 1971, 5125 (1986); 28 5551 (1987); 29 475, 3865, 6537 (1988); 30 4783 (1989); 31 4129 (1990); 32 4337 (1992); 35 385, 389 (1994); 36 7327, 8171, 8175 (1995)
JOC 38 1675 (1973); 43 3205, 3717 (1978); 46 203, 783 (1981); 47 2396 (1982); 50 2690 (1985); 52 547, 674 (1987); 53 3145, 4263 (1988); 55 3902 (1990); 56 4208 (1991); 57 61 (1992); 58 6526 (1993)
J Heterocyclic Chem 17 1333 (1980)
SL 731 (1991); 597 (1995)

X

OR

JOC 45 2739 (1980); 59 2043 (1994)
Syn 235 (1982) (pyridines)
TL 29 475 (1988); 36 7327 (1995)
SL 61 (1994)

OCH₂CH₂OMe

Chem Pharm Bull 33 1016 (1984) (arenes,
pyridines)

OCH₂CH₂NMe₂

Chem Pharm Bull 33 1016 (1984) (arenes,
pyridines)

OCH₂OMe

JACS 79 5792 (1957); 108 7100 (1986); 110 6471
(1988); 111 4522 (1989); 113 5775 (1991)
JOC 44 2480 (1979); 47 2101 (1982) (arenes,
pyridines); 53 3936 (1988); 55 6161 (1990); 58
6692 (1993); 60 1856, 2298 (1995)
Syn 906 (1979)
TL 22 811, 3923 (1981); 24 3795 (1983); 28 5093
(1987); 29 3865, 5765 (1988); 32 4337 (1991); 33
2253 (1992); 35 7537 (1994)
Tetr 39 2031 (1983)
CC 1234 (1986)

OCH₂OR

JACS 101 257 (1979)
JOC 45 2224, 5067 (1980)
TL 36 6197 (1995)

OCH₂OCH₂CH₂SiMe₃

TL 31 4267 (1990); 33 2253 (1992)
Pure Appl Chem 62 2047 (1990)

OCH(CH₃)OEt

JOC 44 2480 (1979)
SL 555 (1990)

OTHP

JACS 70 4187 (1948); 79 5797 (1957); 80 4537
(1958); 107 2712 (1985)
JOC 58 2637 (1993)

OCONEt₂

JOC 48 1935 (1983); 50 5436 (1985) (pyridines); 60
1484 (1995) (indoles)
TL 24 3795 (1983); 28 5093, 5097 (1987); 32 4879
(1991); 33 2253 (1992); 35 7537 (1994)
JACS 107 6312 (1985)
Chem Rev 90 879 (1990) (review)

OPO(NMe₂)₂





TL 27 1391 (1986) (furans)

CH₂OH


Angew Int 17 521 (1978)
JOC 45 1835 (1980); 53 4263 (1988); 55 5202
(1990); 59 2043 (1994)
Ber 113 1304 (1980)
TL 34 3235 (1993)


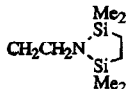
CHROH

Syn 59 (1981)
JACS 115 2042, 5859 (1993)
JOC 59 2219 (1994); 60 1154 (1995)

CR_2OH	JACS 115 10628 (1993)
$\text{CHOHCH}_2\text{NMeR}$	CC 968 (1974)
$\text{CR}(\text{OLi})\text{NR}_2$	Acta Chem Scand 22 1353 (1968) (thiophene) Arkiv Kemi 32 283 (1970) (furan, thiophene) JOC 41 3651 (1976) TL 23 3979 (1982)
CH_2OMe	Syn Commun 5 65 (1975) TL 3973 (1975); 28 5551 (1987); 36 6197 (1995) JOC 48 3653 (1983); 50 2690 (1985); 53 4263 (1988)
$\text{CH}_2\text{OCH}(\text{CH}_3)\text{OCH}_2\text{CH}_3$	JOC 48 3653 (1983)
CPh_2OMe	JACS 74 6282 (1952)
$\text{CH}(\text{OMe})_2$	TL 4921 (1979) JOC 48 3653 (1983); 50 805 (1985)
	TL 27 2963 (1986); 36 8449 (1995)
	JOC 48 3653 (1983)
$\text{CH}_2\text{CH}(\text{OMe})_2$	JOC 48 3653 (1983)
	JOC 48 3653 (1983) SL 61 (1994)
SH	JACS 111 654, 658, 665, 2327 (1989); 117 7261 (1995) TL 36 6619 (1995)
SR	Arkiv Kemi 13 269 (1958) (thiophenes) JOMC 132 321 (1977); 182 155 (1979) JACS 111 658 (1989)
	
CR_2SMe	JACS 101 257 (1979)
SOR	JOC 56 5723 (1991) TL 33 2625 (1992)
SONHPh	JOC 55 74 (1990)
SO_2R	JACS 75 278 (1953) Arkiv Kemi 13 269 (1958) (thiophenes) JOC USSR 5 313 (1969) Tetr 27 433 (1971) JOC 54 24 (1989)
SO_3H	JOC 45 3728 (1980)
SO_3R	Bull Acad Sci USSR, Div Chem Sci 129 (1980) JOC 51 2833 (1986)

X

SO ₂ NHR	JOC 33 900 (1968)
SO ₂ NR ₂	Can J Chem 47 1543 (1969) Angew Int 13 270 (1974) TL 1499 (1975) Bull Acad Sci USSR, Div Chem Sci 129 (1980) Tetr 39 2073 (1983) Syn 822 (1983) (pyridines)
SiR ₂ NR ₂	TL 31 2925 (1990)
NMe ₂	Ber 75 1491 (1942) JOC 31 2047 (1966); 35 1288 (1970); 44 237 (1979) TL 3443 (1970) Org Syn 53 56 (1973) Org Syn Coll Vol 6 478 (1988)
NR ₂	JOC 50 2690 (1985)
NMeCH ₂ CH ₂ NMe ₂	TL 24 5465 (1983)
NHCOC(CH ₃) ₃	JOC 44 1133 (1979); 45 4798 (1980); 46 3564 (1981) (pyridines); 48 3401 (1983) (pyridines); 53 2844, 3513 (1988); 56 6666, 7288 (1991); 58 5537 (1993) J Heterocyclic Chem 17 1333 (1980) Chem Pharm Bull 30 1257 (1982) (arenes, pyridines) Syn 499 (1982) (pyridines) TL 28 5435 (1987); 35 7303 (1994) CC 1528 (1987) SL 360 (1992); 235 (1994)
NHCO ₂ R	JOC 56 6666 (1991)
NHCO ₂ C(CH ₃) ₃	JOC 44 1133 (1979); 45 4798 (1980); 51 2781 (1986); 53 6138 (1988); 54 4549 (1989); 56 7288 (1991); 57 6833 (1992) Syn 499 (1982) (pyridine) TL 28 5093 (1987); 35 7303 (1994)
NRCO ₂ C(CH ₃) ₃	JOC 58 6538 (1993)
NRCO ₂ Li	JOC 56 5045 (1991)
	Helv 57 1988 (1974)
CH ₂ NHMe	JOC 36 1607 (1971)
CH ₂ NR ₂	JACS 85 2467 (1963); 111 5936 (1989) JOC 27 701 (1963); 28 663, 3461 (1963); 32 1479 (1967); 45 5067 (1980); 52 704 (1987); 53 4263 (1988); 60 2298 (1995)

	TL 4159 (1968); 3443 (1970); 22 2797 (1981) JOMC 54 1 (1973) Tetr 39 1975 (1983)
CHMeNMe ₂	TL 32 4569 (1991) JOC 56 4208 (1991)
CH ₂ NRCH ₂ CH(OEt) ₂	TL 31 3125 (1990)
CHRNHSi(<i>i</i> -Bu)Ph ₂	TL 30 5203 (1989)
CH ₂ NHCOC(CH ₃) ₃	TL 29 4277 (1988)
CH ₂ NHCONMe ₂	TL 34 6263 (1993)
CH=NR	JOC 41 1564 (1976); 45 5067 (1980); 58 2463 (1993) JOC 44 2004 (1979) JACS 110 4346 (1988) SL 729 (1991); 609 (1994)
	TL 603 (1966); 3443 (1970); 27 1971 (1986) Chem Ind 120 (1967) Austral J Chem 21 2319 (1968) Acta Chem Scand B 31 514 (1977)
(CH ₂) ₂ NMe ₂	TL 29 3865 (1988)
	TL 32 1965 (1991)
CH ₂ CH ₂ NHCOC(CH ₃) ₃	TL 32 1963 (1991)
CH(CO ₂ H)CH ₂ NHCOC(CH ₃) ₃	TL 26 1777 (1985) (furans, thiophenes); 36 881 (1995) JOC 59 4042 (1994)
CO ₂ H	JOC 53 2728 (1988)
CO ₂ R	JOC 29 853 (1964); 40 1427 (1975); 44 4463 (1979); 46 2799 (1981); 47 34 (1982); 50 4362 (1985); 51 2011 (1986); 54 2964, 4549 (1989); 57 2700 (1992); 58 7330, 7587 (1993); 60 6588 (1995) CC 564 (1968); 1552 (1970); 1042 (1980) TL 4159 (1968); 2559, 3965 (1978); 22 1779 (1981); 23 1647 (1982); 25 2127 (1984) (pyridines); 27 501 (1986); 32 3845 (1991); 35 3949 (1994) J Heterocyclic Chem 6 475 (1969) Tetr 27 6171 (1971); 39 1983 (1983) Chem Ind 75 (1974); 519 (1975) Syn 797 (1975); 127 (1981) (pyridines) Ind J Chem B 15 512 (1977) JACS 103 4247 (1981); 111 4522 (1989); 115 5843, 10628 (1993) JCS Perkin I 2227 (1982)
CONHR	

X

CONHMe

JOC 58 3643 (1993)

CONR₂

JOC 41 3651 (1976); 42 1823 (1977); 44 4463, 4802 (1979); 47 34, 2120, 3335, 5009 (1982); 48 1565 (1983); 49 318 (1984); 50 805, 2690, 4362, 5902 (1985); 51 271, 2011, 3325, 3566 (1986); 52 183, 283, 674, 3181 (naphthalenes), 5668 (1987); 53 223, 2728 (1988); 54 4372, 4386, 4715 (1989); 55 1375 (1990); 56 1683 (1991); 58 5858, 7158 (1993); 59 7161 (1994); 60 2298, 8417 (1995)

TL 5099, 5103, 5107 (1978); 21 3335, 4739 (pyridines) (1980); 22 1093, 2349 (1981); 24 2649 (pyridines), 2945, 3795, 4515, 4735 (pyridines) (1983); 26 1149 (thiophenes), 6213 (1985); 28 5093, 5097 (1987); 30 5837, 5841 (1989); 32 4883, 7179 (1991); 33 6775 (1992) (E⁺ = 1-nitrocyclohexene); 35 401 (1994); 36 1039 (1995) (cuprates)

Can J Chem 57 1598 (1979)

Heterocycles 14 1649 (1980) (review)

JACS 102 1457 (1980); 104 5531 (1982); 107 6312 (1985); 108 7100 (1986); 109 3402 (1987); 110 6471 (1988); 111 4829 (1989); 115 10628 (1993); 116 11723 (1994)

CC 1215 (1981)

Acct Chem Res 15 306 (1982) (review)

Tetr 39 1955, 1983 (1983)

Chem Rev 90 879 (1990) (review)

SL 313 (1990)

CSNHR

JOC 41 4029 (1976)

CN

Arkiv Kemi 21 335 (1963) (thiophene)

BSCF 628 (1976) (thiophene, selenophene)

JOC 47 2681 (1982) [*m*-C₆H₄(CN)₂]

JOC 40 2008, 3158 (1975); 42 2649 (1977) (thiophenes); 43 727 (1978); 44 4464 (1978); 46 3881 (1981); 47 1585, 2633 (pyridines), 2837 (1982); 52 713 (1987); 60 2298 (1995)

Angew Int 15 270 (1976)

Heterocycles 11 133 (1978) (pyridines)

TL 227 (1978); 21 3335 (1980); 23 2091 (1982); 24 3795 (1983); 26 5335 (1985); 27 3431 (1986)

JCS Perkin I 1343 (1982); 173 (1985)

JACS 104 4015 (1982); 108 2662, 4138 (furan) (1986)

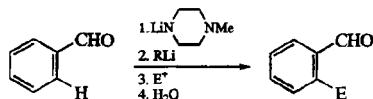
Tetr 40 2107 (1984)



CC 388 (1986)

SL 347 (1994)

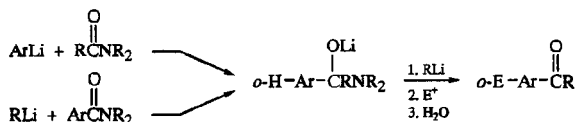
Tetr 39 3593 (1983) (furans)



TL 23 3979 (1982); 34 6173, 6993 (1993); 35 5369 (1994)

JOC 49 1078 (1984); 52 104 (1987); 53 3936 (1988); 54 3730 (1989); 55 69 (1990); 57 1593 (1992)

SL 615 (1992) (review)



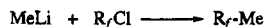
Acta Chem Scand 22 1353 (1968) (thiophene)

Arkiv Kemi 32 283 (1970) (furan, thiophene)

JOC 41 3651 (1976)

TL 24 5465 (1983); 27 1793 (1986); 35 5331 (1994)

SL 615 (1992) (review)



JOC 57 4749 (1992)



R = allylic, benzylic

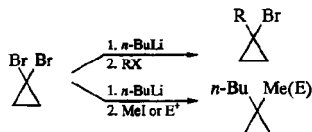
JACS 91 4871 (1969)

TL 4115 (1973); 2215 (1974)

JOC 39 1168, 3452 (1974)

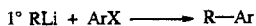


JACS 110 1305 (1988)



JACS 97 949 (1975)

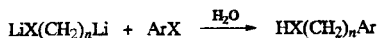
BCSJ 50 2158 (1977)



JACS 91 4871 (1969)

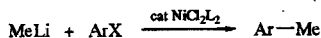
JOC 39 3452 (1974); 60 4542 (1995)

TL 33 6183 (1992)

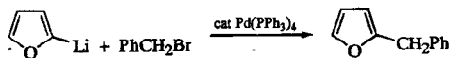


$\text{X} = \text{PhCON} (n = 2, 3); \text{OCR}_2 (n = 2, 4)$

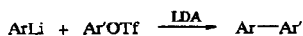
JOC 58 5976 (1993)



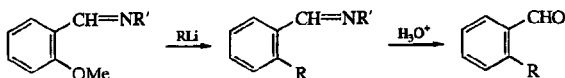
JACS 97 7262 (1975)



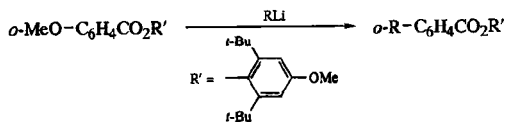
Syn 51 (1987)



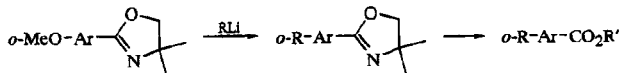
JOC 58 4722 (1993)



TL 34 3255 (1993)



TL 36 4821 (1995)

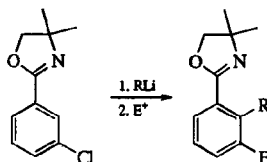


JACS 97 7383 (1975); 104 881 (1982); 114 1010 (1992) (also Me₂N substitution)

JOC 43 1372 (1978)

TL 32 3213, 3871 (1991)

See also page 101, Section 2.3.



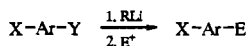
$E^+ = H^+, RI, RCHO, DMF, RCOCl, RNCO, CO_2$

JACS 110 7178 (1988)



$X = F, OR$

JACS 114 8732 (1992)



Review: Acct Chem Res 15 300 (1982)

$X = H, R, Br, CH_2Cl, CHClCH_3, CCl(CH_3)_2, CH_2CH_2Br, (CH_2)_3Cl(Br), (CH_2)_2CHBrCH_3,$
 $OR, O(CH_2)_nBr (n = 2, 3), OH, CR_2OH, CH_2CH_2OH, CH_2SH, CH(OLi)NR'_2, CN,$
 $CR_2CN, CH_2CH_2CN, CO_2R, CO_2H, CH_2CO_2H, (CH_2)_2CO_2H, NO_2, NH_2, NHCOR,$
 $CH_2NR_2, SH, SO_2NR_2, pyrrole$

$Y = Br, I$

$E^+ = H_2O, D_2O, Br_2, RX, epoxide, RCHO, R_2CO, RCO_2H, RCO_2R, RCOCl, HCONR_2,$
 $RCONR_2, CO_2, RCN, PhNCO, imines, Michael acceptors$

Ber 71 1903 (1938); 73 1197 (1940); 103 1412 (1970)

JOC 3 108 (1938); 37 1545 (1972); 39 2051, 2053 (1974); 40 2394 (1975); 41 1184, 1187, 1268, 2628, 2704 (1976); 42 257 (1977); 43 1606, 3800 (1978); 45 922 (1980); 46 327, 1057, 1384, 2730, 2826, 4600, 4608, 4804 (1981); 47 2608 (1982); 50 2423, 2427 (1985); 51 3973, 5100 (indoles) (1986); 52 586, 704, 5668 (1987); 53 2943, 5484 (1988); 54 4280 (1989); 56 2914, 4325, 5723 (1991); 57 40, 5937, 6783 (1992); 58 4083, 7330 (1993)

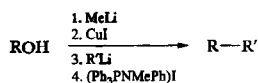
JACS 61 106, 1371 (1939); 62 344, 346, 446, 1843, 2327 (1940); 63 1553, 2844 (1941); 64 1007 (1942); 69 1537 (1947); 70 4177 (1948); 99 4822 (1977); 106 7150 (1984); 111 2984, 5936 (1989); 113 4303, 5085 (1991)

TL 4573 (1977); 22 1475, 3707, 4213 (1981); 28 1937, 2933, 4507, 6089 (1987); 29 4385, 6425 (1988); 30 275 (1989) (intramolecular); 34 2043 (1993); 35 1747 (1994)

Org Prep Proc Int 10 267 (1978)

JOMC 212 1 (1981); 215 281 (1981)

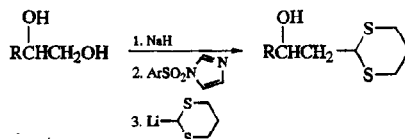
Syn Commun 12 49, 231 (pyrroles) (1982)



R = allylic, benzylic, cyclopropylcarbinyl

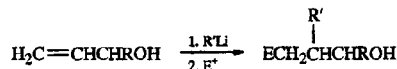
R' = 1° alkyl, aryl, alkynyl

JACS 99 2361 (1977)



JOC 60 8122 (1995)

For other organometallics, see page 392, Section 22 and page 585, Section 1.



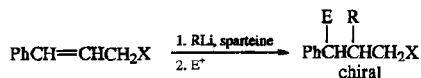
E⁺ = H₂O, RX, RCHO, CO₂

TL 711 (1969)

JOC 37 4236 (1972)

Org Syn Coll Vol 6 786 (1988)

SL 671 (1990)



X = OH, OR, NHR, NR₂, CH₂OH; E⁺ = H⁺, RX, RSSR, CO₂

JOC 59 2925 (1994)

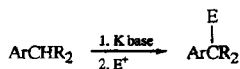
JACS 117 8853 (1995)



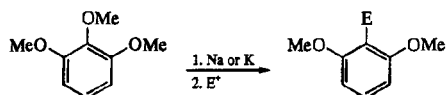
E⁺ = H₂O, D₂O, R₂CO, CO₂

TL 875 (1966)

2.2. Organosodium or -Potassium Compounds



E^+	
D ₂ O	JACS 106 361 (1984)
MeI	Helv 59 453 (1976) TL 25 741 (1984)
epoxide	JOC 58 4656 (1993) TL 34 801 (1993)
CO ₂	JACS 85 3984 (1963) SL 119 (1991)

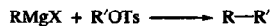


$E^+ = D_2O, RX, RCHO, RCOCl, ClCO_2R, HCO_2R, ClCONR_2, CO_2, X_2, Me_3SiCl$

JOC 55 5386 (1990); 57 3101 (1992)
TL 34 5635 (1993)

2.3. Grignard Reagents

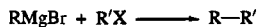
Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.6, p 241



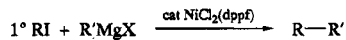
Org Syn Coll Vol 1 471 (1932); 2 47 (1943)



Org Syn Coll Vol 1 186 (1941)
TL 1393 (1969)



TL 1857 (1978) (R = 1° alkyl)
JOC 53 729 (1988) (R = 3° alkyl)

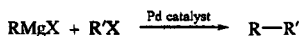


R' = 1° alkyl, aryl

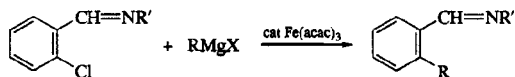
TL 32 189 (1991)
JOC 60 5102 (1995)

	$\text{RMgX} + \text{ArY} \xrightarrow{\text{Ni catalyst}} \text{R}-\text{Ar}$	
<u>Y</u>	<u>R</u>	
halogen	1°, 2° alkyl	<p>IACS 94 4374 (1972); 97 7262 (1975); 114 5269 (1992) JOMC 50 C12 (1973) Helv 56 460 (1973) J Heterocyclic Chem 10 243 (1973) TL 3 (1974); 34 2111 (1993); 36 8449 (1995) BCSJ 49 1958 (1974) Tetr 38 3347 (1982); 39 2699 (1983) JOC 47 4319 (1982); 50 5370 (1985); 53 5564 (1988); 54 1523 (1989) Org Syn Coll Vol 6 407 (1988) J Heterocyclic Chem 10 243 (1973); 12 443 (1975) Tetr 38 3347 (1982) JOC 47 4319 (1982); 54 1523 (1989)</p>
	benzylic	<p>JACS 94 4374 (1972); 106 3286, 7150 (1984); 110 8153 (1988); 113 7064 (1991) CC 144 (1972) BCSJ 49 1958 (1974); 55 845 (1982) J Heterocyclic Chem 12 443 (1975) CL 133 (1975) JOC 41 2252 (1976); 47 4319 (1982); 50 2086 (1985); 51 142, 921 (1986); 54 1523 (1989); 58 1415, 6692, 7516 (1993); 60 3568, 8101 (1995) TL 23 4629 (1982); 30 215, 3513 (1989); 33 1675, 7553 (1992); 35 9063 (1994) Tetr 38 3347 (1982) Chem Pharm Bull 30 802, 2369 (1982)</p>
	aryl	
OCONEt ₂	Me Me ₃ SiCH ₂ , Ph	<p>JOC 57 4066 (1992) JOC 57 4066 (1992); 60 1484 (1995)</p>
OMs	Me, Ar	JOC 60 6895 (1995)
OTf	Me, <i>n</i> -Bu, Me ₃ SiCH ₂ , Ph	JOC 57 4066 (1992)
OPO(OR) ₂	1° alkyl, aryl	TL 22 4449 (1981)

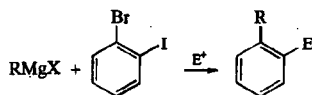
SH	Me, Ph	CC 637 (1979)
SR	Me, Ar	CC 637 (1979) TL 23 4629 (1982); 26 39 (1985)
SOR	Me, Ar	CC 637 (1979)
SO ₂ R	Me, Ar	CC 637 (1979)



<u>R</u>	<u>R'X</u>	
1°, 2° alkyl	1°, 2° RI ArX	TL 27 6013 (1986) JOMC 118 349 (1976) TL 1871 (1979); 21 845 (1980) IACS 104 180 (1982); 106 158 (1984)
aryl	1° RI ArX	TL 27 6013 (1986) JOMC 118 349 (1976); 125 281 (1977) TL 21 845 (1980); 22 5319 (1981) CC 511 (1984) TL 35 1909 (1994) JACS 117 9101 (1995) (chiral)
	ArX·Cr(CO) ₃ ArOTf	

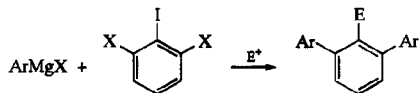


JOC 54 1523 (1989)



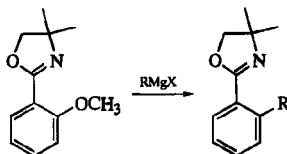
R = aryl, alkenyl, alkynyl; E⁺ = H₂O, HCONR₂, CO₂, I₂

TL 26 29 (1985); 29 881, 885 (1988); 34 8317 (1993)
JOC 50 3104, 5524 (1985); 51 3162 (1986); 52 4311 (1987); 53 3555 (1988); 56 5630 (1991); 58 964 (1993)



E⁺ = H₂O, Br₂, I₂, RNCO; X = Cl, Br

JOC 51 3162 (1986); 55 881 (1990); 57 2721 (1992)
TL 36 8403 (1995)



JACS 97 7383 (1975); 104 879, 881 (1982); 107 682, 4238 (1985); 109 3098, 5446 (1987); 112 8090 (1990)

JOC 43 1372 (1978); 46 783 (1981); 53 1003 (1988); 58 4398 (1993); 60 5702 (1995)

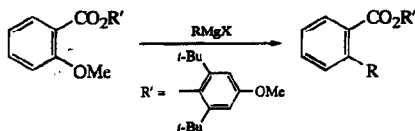
Syn Commun 10 17 (1980)

Tetr 44 3107 (1988)

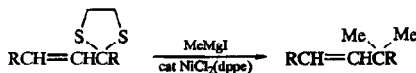
SL 697 (1990)

TL 33 853 (1992); 34 6185, 6989, 6993, 7401 (1993)

See also page 88, Section 2.1 for analogous Li reactions.

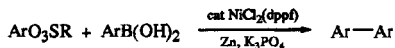


TL 36 4821 (1995)

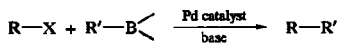


JOC 57 4550 (1992)

2.4. Organoboron Reagents



JOC 60 1060 (1995)



Review: Chem Rev 95 2457 (1995)

$\text{R}-\text{X}$

ArCH_2X

$\text{ArBr}(\text{I})$

$\text{R}'-\text{B}$

$\text{ArB}(\text{OH})_2$

$\text{ArB}(\text{OR})_2$

$(\text{ArBO})_3$

R_3B

JOC 59 6501 (1994)

TL 36 3051 (1995)

TL 32 5881 (1991)

JOC 59 33 (1994)

TL 27 6369 (1986)

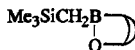
JACS 111 314 (1989)



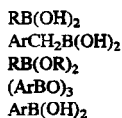
TL 27 6369 (1986); 33 6919 (1992)
 JACS 111 314 (1989)
 SL 687 (1991); 727 (1992)
 JOC 58 2201 (1993)



TL 31 5541 (1990)



TL 31 4981 (1990)



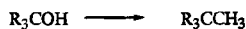
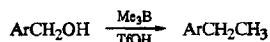
JOC 59 6501 (1994)
 JOC 59 6501 (1994)
 CL 1405 (1989)
 JOC 59 3917, 5034 (1994)
 Syn Commun 11 513 (1981)
 Organomet 3 1261 (1984)
 JOC 49 5237 (1984); 53 2052
 (1988); 55 4581 (1990); 56 3763
 (1991); 57 1015, 1653 (1992); 58
 6692, 7832 (1993); 59 6095,
 6391, 6501, 8151 (1994); 60 264,
 292, 748, 1924, 3578, 7030
 (1995)
 Chem Scripta 24 5 (1984)
 TL 26 5997 (1985); 28 5093, 5097
 (1987); 29 2135, 2517, 5459,
 5463 (1988); 31 1523 (1990); 32
 2229, 2273, 4879, 4883, 5277
 (1991); 33 2253, 2773, 6679
 (1992); 34 2127, 2437, 2933,
 2937, 5125, 7637, 7917, 8237
 (1993); 35 1909, 2003, 2705,
 3277, 6489, 8747, 9177 (on
 polymer) (1994); 36 1679, 6695
 (1995)
 JACS 111 3744 (1989); 112 4324,
 4592 (polymer), 8024 (1990);
 114 1018, 6227, 10775 (1992);
 116 7895, 10847, 11723 (1994)
 SL 207, 354, 715 (1992); 93 (1994);
 765, 1040 (1995)
 Acta Chem Scand 47 221 (1993)
 (review)



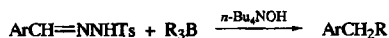
CL 1405 (1989)
 JOC 56 1683, 6787 (1991); 59 5034
 (1994)
 TL 32 5881 (1991); 35 2919 (1994)
 SL 207 (1992)
 JACS 115 4935 (1993) (polymers)
 Gazz Chim Ital 120 779 (1990)
 TL 35 9063 (1994)
 JOC 60 264, 292, 7491 (1995)



<u>R-X</u>	<u>R'-B</u>	
ArX·Cr(CO) ₃	ArB(OH) ₂	TL 35 1909 (1994)
ArOTf	RB(OH) ₂	SL 283 (1995)
	R ₃ B	SL 283 (1995)
	RB	JOC 58 2201 (1993) (inter- and intramolecular)
	ArB(OH) ₂	SL 221 (1990); 283 (1995)
		Tetr 45 6679 (1989)
		TL 31 1665 (1990); 34 5635 (1993); 35 3277, 7621 (1994)
		SL 221 (1990); 283 (1995)
		JOC 57 379 (1992); 58 2001 (1993); 59 6084, 6095 (1994); 60 1060 (1995)
	ArB(OR) ₂	SL 221 (1990)
		TL 32 5881 (1991)
		JOC 58 2001 (1993)
	NaBAr ₄	TL 33 4815 (1992)

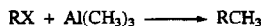


JOC 56 2759 (1991)



JOC 59 5530 (1994)

2.5. Organoaluminum Reagents

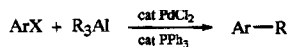


JOC 35 532 (1970)

JACS 110 1303, 8591 (1988)



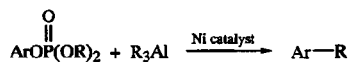
JOC 55 3697 (1990)



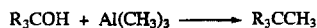
JOC 57 5268 (1992)



JCS Perkin I 2513 (1989)



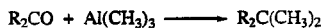
TL 22 4449 (1981)



CC 595 (1972)

Austral J Chem 27 1639 (1974)

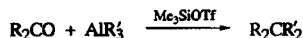
JOC 60 6557 (1995)



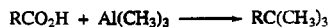
CC 595 (1972)

Austral J Chem 27 1655 (1974)

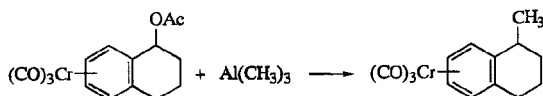
JACS 112 8902 (1990)



TL 35 3017 (1994)

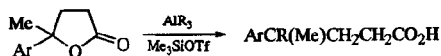


CC 595 (1972)



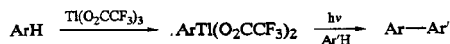
TL 26 767 (1985); 35 6861 (1994)

JACS 113 5402 (1991)

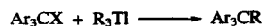


TL 35 3017 (1994)

2.6. Organothallium Reagents

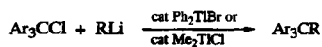


JACS 92 6088 (1970)



R = Me, Ph

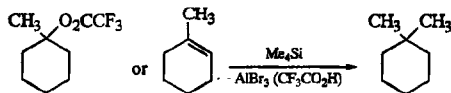
SL 235 (1991)



R = Me, Ph

TL 32 2255 (1991)

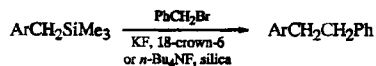
2.7. Organosilicon Reagents



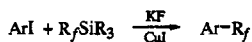
CC 748 (1980)



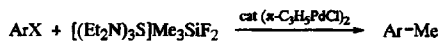
JOC 55 3486 (1990)



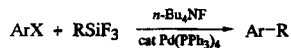
TL 23 577 (1982)



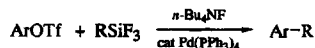
TL 32 91 (1991)



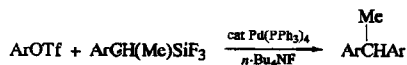
TL 29 97 (1988)



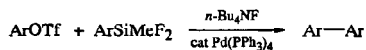
TL 35 6507 (1994)



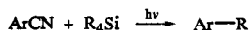
TL 31 2719 (1990)



JACS 112 7793 (1990)



TL 31 2719 (1990)



TL 31 6395 (1990)

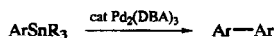
2.8. Organogermanium Reagents



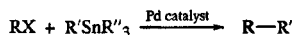
TL 31 6395 (1990)

2.9. Organotin Reagents

See also page 117, Section 2.22.



JOC 58 5434 (1993)



Reviews:

Angew Int 25 508 (1986)

JOMC 304 1 (1986)

Syn 803 (1992)

RXArCH₂BrR'

1° alkyl

JACS 101 4992 (1979)

TL 27 5207 (1986)

benzylic

JACS 101 4992 (1979)

aryl

JACS 101 4992 (1979)

SL 771 (1993) (intramolecular)

heterocyclic

JOC 59 4250 (1994)

TL 36 6507 (1995)

ArBr(I)

1° alkyl

JACS 101 4992 (1979); 114

4128, 6556 (1992)

Proc Acad Sci USSR, Chem Sec

272 333 (1983)

TL 36 125, 3111 (1995)

benzylic

TL 34 23 (1993)

aryl

JACS 101 4992 (1979); 111

3744 (1989)

JOC USSR 17 18 (1981)

Proc Acad Sci USSR, Chem Sec

272 333 (1983)

JOC 57 1593, 1653 (1992); 59

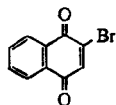
4285, 5905 (1994); 60 12,

523, 5814 (1995)

TL 35 481, 5613 (1994); 36 125,

3111, 3409 (1995)

<u>RX</u>	<u>R'</u>	
ArBr(I) (<i>continued</i>)	heterocyclic	TL 27 4407 (1986); 30 4249 (1989); 34 2127, 2933 (1993); 35 2405 (1994); 36 919, 2191, 5247, 6507 (1995) SL 771 (1993) JOC 59 4250, 5905 (1994); 60 5814, 6218 (1995) JACS 117 12426 (1995)
(OC) ₃ Cr·ArX	1° alkyl heterocyclic	CC 1755 (1987) TL 28 2645 (1987)
Het-X (X = Cl, Br, I)	1° alkyl benzylic aryl	SL 1227 (1995) TL 35 3155 (1994) TL 29 2135 (1988); 34 2127 (1993); 35 3155 (1994); 36 1945, 2191, 3111 (1995) SL 415, 1227 (1995) JACS 112 5662 (1990); 113 7064 (1991) TL 32 4263 (1991); 33 2199 (1992); 34 2937, 7919 (1993); 35 2405, 3155 (1994); 36 1945, 2615 (1995) SL 771 (1993); 235 (1994); 147, 415, 1227 (1995) JOC 59 4250 (1994); 60 748, 2082, 3487, 5899, 6218, 6813 (1995)
	heterocyclic	JACS 112 5662 (1990); 113 7064 (1991) TL 32 4263 (1991); 33 2199 (1992); 34 2937, 7919 (1993); 35 2405, 3155 (1994); 36 1945, 2615 (1995) SL 771 (1993); 235 (1994); 147, 415, 1227 (1995) JOC 59 4250 (1994); 60 748, 2082, 3487, 5899, 6218, 6813 (1995)
ArOSO ₂ F	aryl	JOC 56 3493 (1991)
ArOTf	1° alkyl	JACS 109 5478 (1987) TL 31 2357, 3421, 5189 (1990); 34 5635 (1993) JOC 57 678 (1992); 58 5434 (1993)
	aryl	JACS 109 5478 (1987) TL 31 2357, 3421, 5189 (1990) SL 709 (1991) JOC 57 678 (1992); 58 1963, 5434 (1993); 59 1216, 4285 (1994)
	heterocyclic	JOC 59 4250 (1994) TL 35 2405 (1994) JACS 117 12426 (1995)
ArO ₃ SC ₆ H ₄ F- <i>p</i>	1° alkyl, aryl	JOC 57 6321 (1992)
Het-OTf	aryl	JACS 109 5478 (1987) JOC 56 3497 (1991); 58 403 (1993); 59 6902 (1994); 60 5069 (1995)

$(\text{ArN}_2)\text{X}$ 

heterocyclic

TL 32 4263 (1991); 34 7919
(1993); 35 2405 (1994); 36
2615, 5319 (1995)
JOC 60 292 (1995)

1° alkyl

JOC 48 1333 (1983)

aryl

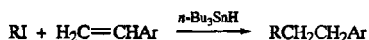
JOC 48 1333 (1983)

1° alkyl, aryl

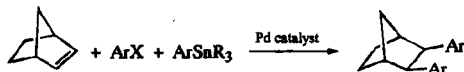
JOC 59 6075 (1994)



TL 31 6395 (1990)



TL 35 4243 (1994)



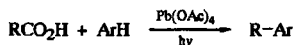
Tetr 45 961 (1989)

BCSJ 66 3522 (1993)

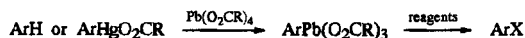
CL 1443 (1994)

SL 1225 (1995)

2.10. Lead Reagents



JACS 111 8943 (1989)

X

Ar'

 CR_2NO_2 CH(COR)_2 $\text{CH(COR)CO}_2\text{R}$ $\text{CR(CO}_2\text{R)}_2$ Reagent(s)Ar'H, $\text{CF}_3\text{CO}_2\text{H}$, (AlCl_3) R_2CHNO_2 RCOCH_2COR $\text{RCOCH}_2\text{CO}_2\text{R}$ $^-\text{CR(CO}_2\text{R)}_2$

Austral J Chem 32 1531 (1979)

TL 22 783 (1981)

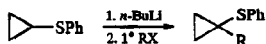
See page 1522, Section 20.

See page 1528, Section 22.

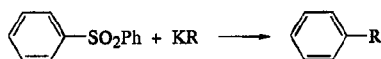
See page 17, Section 2.

2.11. Sulfur Reagents

See also page 77, Section 1.

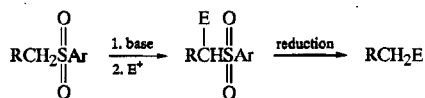


TL 23 2379 (1982)



R = *t*-Bu, PhCH₂

TL 25 4851 (1984)



E^+

RX

BSCF 3065 (1973); 1363 (1975)

Teur 37 1233 (1981)

JCS Perkin I 1846 (1981)

CL 1711 (1981)

JACS 106 3811 (1984); 108 1035 (1986)

JOC 52 3541 (1987); 60 1828 (1995)

TL 28 813, 6069 (1987); 31 5575 (1990)

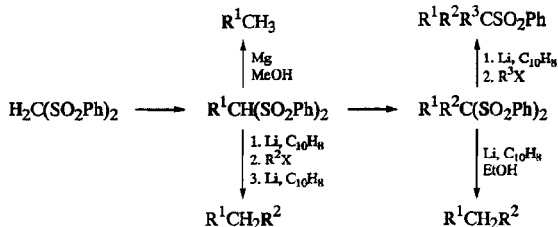
epoxide

TL 2275 (1975)

BSCF 513 (1976)

RCO₂R

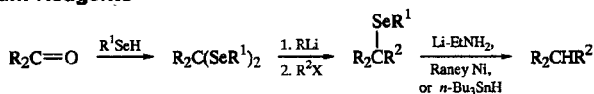
JOC 45 4002 (1980)



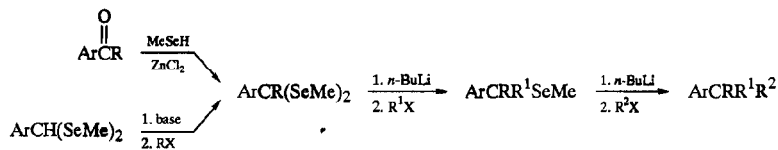
JOC 50 1749 (1985); 55 247 (1990); 58 5892 (1993)

N. S. Simpkins, "Sulphones in Organic Synthesis," Pergamon, New York (1993) (review)

2.12. Selenium Reagents



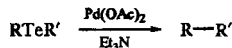
TL 2643 (1976); 28 1337 (1987)



TL 27 1719, 1723 (1986)

CC 457 (1986)

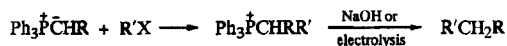
2.13. Tellurium Reagents



R, R' = 1°, 3° alkyl; aryl

TL 29 3533 (1988)

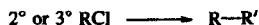
2.14. Phosphorus Reagents



Ann 704 109 (1967)

2.15. Organotitanium and -zinc Reagents

See also page 122, Section 2.25.



R'ZnX

JOC 53 729 (1988)

R'_2Zn

CC 1202 (1980)

(CH_3)_2Zn, (cat) TiCl_4

Angew Int 19 900, 901 (1980)

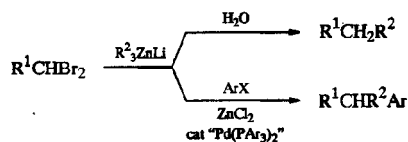
Syn Commun 11 261 (1981)

CH_3TiCl_3

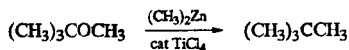
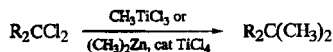
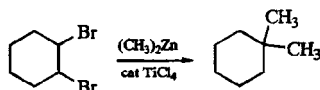
Angew Int 19 900, 901 (1980)

(CH_3)_2TiCl_2

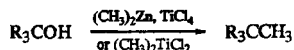
Angew Int 19 900, 901 (1980)



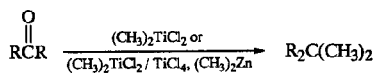
TL 32 1573 (1991)



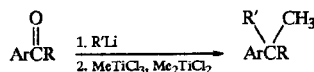
Syn Commun 11 261 (1981)



CC 237 (1981)

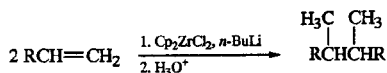


CC 237 (1981)
JOC 48 254 (1983)

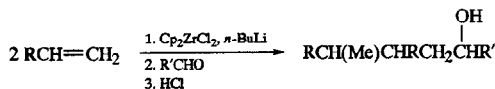


JOC 48 254 (1983)

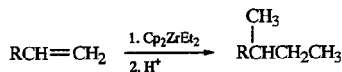
2.16. Organozirconium Reagents



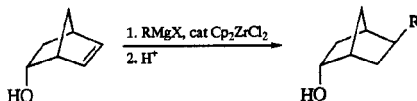
TL 34 2243 (1993)
SL 451 (1994), 1237 (1995) (both intramolecular)



TL 35 695 (1994)

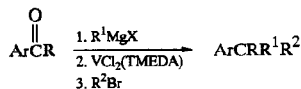
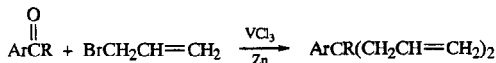


JOC 54 3521 (1989)
JACS 113 6266, 6268 (1991)
TL 32 6797 (1991)



JACS 114 6692 (1992)

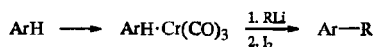
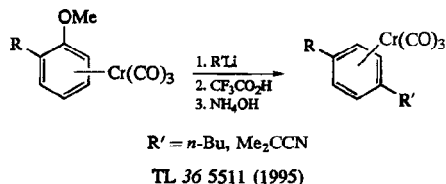
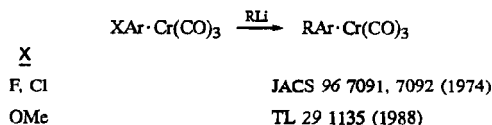
2.17. Vanadium Reagents



R² = allylic, PhCH₂, CH₂C≡CH (alkyne and allene product)

TL 36 6495 (1995)

2.18. Organochromium Reagents



RLi = R'Li (R' = alkyl, vinylic, aryl, allylic, alkynyl), LiCr₂CN,
LiCH(OR)CN, LiCH₂CO₂R, LiCH₂COR, LiCH(SR)₂

JACS 97 1247 (1975); 98 6387 (1976); 99 959, 1675 (1977); 101 217, 3535 (1979); 111 1804 (1989); 113 5402 (1991)

JOC 44 3275 (1979)

Tetr 37 3957 (1981)

Pure Appl Chem 53 2379 (1981) (review)

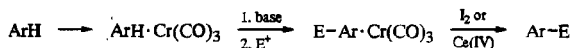
JOMC 221 147 (1981); 226 183 (1982); 240 C5 (1982) (heterocycles)

CC 1359 (1982)

Organomet 2 467 (1983)

TL 29 3223 (1988)

SL 657 (1991)



E⁺ = RX, CO₂, RCHO, Me₃SiCl, RO₂CCl, PhSCl, HCONMe₂, ClCONMe₂, B(OR)₃

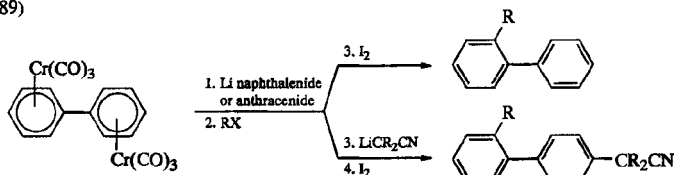
JACS 101 769 (1979)

JOC 45 2555, 2560 (1980); 56 7199 (1991); 57 3563, 6487 (1992); 58 1238, 6182 (1993); 59 1961 (1994)

TL 21 2069 (1980); 23 1605 (1982); 27 5525 (1986); 35 3497, 6159 (1994); 36 5515 (1995) (chiral base)

CC 1260 (1981) (indoles); 467 (1982) (indoles); 1235 (1986)

SL 59 (1989)

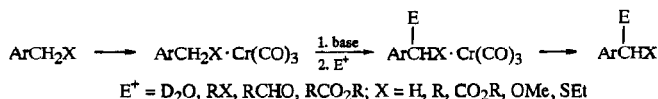


Organomet 6 699 (1987)

JOC 52 4827 (1987)

JACS 112 8388 (1990)

TL 32 3341 (1991)



JACS 94 2897 (1972); 106 2207 (1984)

CC 813 (1975); 1264 (1981); 1316 (1983)

TL 2727 (1975); 34 6259 (1993); 35 6861 (1994)

Tetr 35 2249 (1979)

BSCF II 357 (1982)

S. J. Coote, S. G. Davies and C. L. Goodfellow, "Advances in Metal-Organic Chemistry," Ed. L. S. Liebeskind, JAI Press, Greenwich, CT (1991), Vol 2 (review)



$\text{R} = 3^\circ \text{ alkyl, allylic, benzylic}$

TL 22 5167 (1981)

JOC 52 511 (1987)

2.19. Organomanganese Reagents



RM

RLi ($\text{R} = \text{Me}, \text{Ph}$)

JCS Dalton 1683 (1975)

RMgX ($\text{R} = \text{Me}, \text{Ph}$)

Organomet 1 1053 (1982)

RCOCH_2Li

Organomet 1 1053 (1982)

2.20. Organoiron Reagents

See page 101, Section 2.3, for the iron catalyzed cross-coupling of RMgX and ArX .

2.21. Organonickel Reagents



$\text{X} = \text{electron-donating}; \text{Y} = \text{electron-withdrawing}$

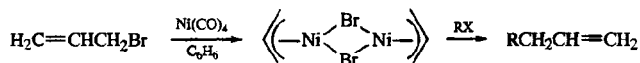
$\text{Ni}(\text{OAc})_2$, NaH, NaO-*t*-Am, bipy, KI

TL 29 545 (1988)

JOC 54 4844 (1989)

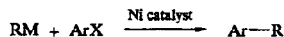
cat NiCl_2 , Zn, cat PPh_3 , py

SL 371 (1994)



$\text{R} = \text{alkyl, vinylic, aryl}$

See page 382, Section 20.

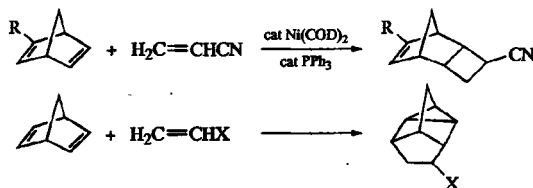


Reviews:

Pure Appl Chem 52 669 (1980)

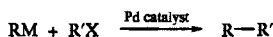
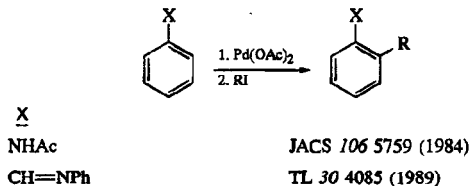
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.5, p 207

For M=Li, see page 88, Section 2.1; M=Mg, see page 101, Section 2.3; M=Al, see page 106, Section 2.5; M=Zn, see page 122, Section 2.25.



X = CHO, COR, CN, SOR, SO₂R
 JOC 56 3761 (1991)
 JACS 117 10276 (1995)

2.22. Organopalladium Reagents

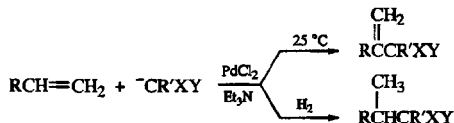


Reviews:

Pure Appl Chem 52 669 (1980)

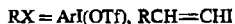
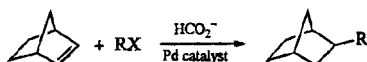
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.5, p 207

For M=Li, see page 88, Section 2.1; M=Mg, see page 101, Section 2.3; M=B, see page 104, Section 2.4; M=Sn, see page 109, Section 2.9; M=Cu, see page 118, Section 2.23; and M=Zn, see page 122, Section 2.25.



X, Y = COR, CO₂R; CO₂R, CO₂R; H, CN

See page 1528, Section 22; page 1724, Section 2;
 and page 1801, Section 6, respectively.

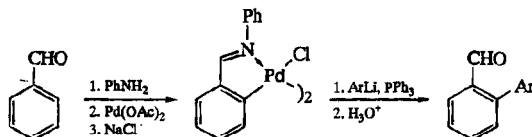


CC 1368 (1989)

JOMC 368 249 (1989)

TL 34 7493 (1993); 36 2051 (1995) (chiral)

SL 291 (1994)



TL 35 5039 (1994)

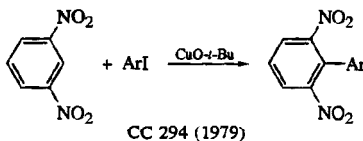
2.23. Organocopper Reagents

Reviews:

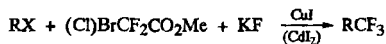
Syn 63 (1972)

Org Rxs 22 253 (1975); 41 135 (1992)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 3, Part 1.5, p 207



CC 294 (1979)



TL 32 7689 (1991) (R = allyl, benzyl, aryl, vinylic); 34 4241 (1993) (R = alkyl)



Cu

Syn 9 (1974) (review)

Tetr 38 2569 (1982) (intramolecular)

TL 31 5405 (1990)

JACS 113 8118 (1991); 114 1018, 5729 (1992); 115 5330 (1993)

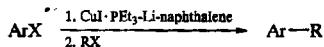
SL 827 (1991)

Cu, cat PdCl₂ or PdCl₂(PPh₃)₂ or Pd(PPh₃)₄

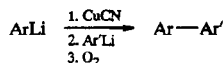
TL 34 3421 (1993)

Cu, cat Pd(P-o-Tol₃)₄

JOC 49 5237 (1984)



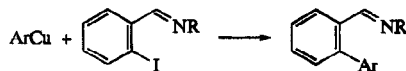
JOC 53 4482 (1988)



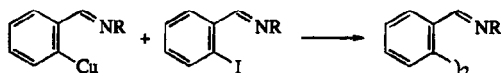
JACS 113 8161 (1991); 115 9276 (1993); 117 10889 (1995)

Tetr 48 2579 (1992)

TL 34 2225 (1993); 35 815, 7553 (1994)

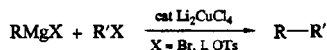


JOC 59 3497 (1994)



JACS 98 8282 (1976)

Org Syn Coll Vol 8 586 (1993)



Syn 303 (1971)

JACS 96 7101 (1974); 109 7477 (1987); 110 8117 (1988); 111 3439 (1989)

Angew Int 13 82 (1974)

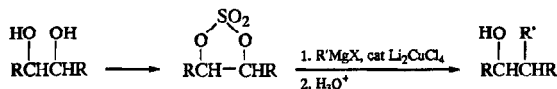
JOC 41 3505 (1976); 52 2337, 4369 (1987); 53 1790, 1922 (1988); 54 1948 (1989); 56 1386 (1991); 58 4567, 5964 (1993); 59 6322 (1994)

TL 4697 (1976); 23 3115, 3587 (1982); 27 3903, 6193 (1986); 28 651, 1175 (R'X = allylic acetate), 2281 (1987); 36 7285 (1995)

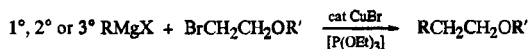
Ber 111 1446 (1978)

Ann 1532 (1982)

J Chem Res (S) 93 (1982)

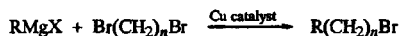


JACS 110 7538 (1988)



R' = H, alkyl, Ac

TL 3263 (1977)



Cu catalyst

R

n

CuBr, HMPA

i-Pr, Ar

3-6

BCSJ 59 2035 (1986)

Ar

3

JOC 60 8081 (1995)

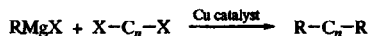


<u>Cu catalyst</u>	<u>R</u>	<u>n</u>	
	Ar	4	JACS 114 6621 (1992) JOC 58 6349 (1993)
CuBr, LiBr, LiSPh	Ar	3	TL 35 5189 (1994)
Li ₂ CuCl ₄	Ar	3	JOC 58 6526 (1993) TL 35 5189 (1994)
	ArCH ₂	6	JOC 59 2616 (1994)

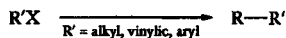
RM

RMgX, cat CuBr (R = 1° alkyl, allylic, aryl) TL 30 1281, 3999 (1989)
JOC 55 4417 (1990)


R₂CuLi (R = Me) TL 30 3999 (1989)

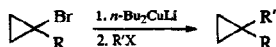


<u>Cu catalyst</u>	<u>R</u>	<u>X</u>	<u>n</u>	
CuBr, HMPA	<i>i</i> -Pr, Ar	Br	3-6	BCSJ 59 2035 (1986)
CuBr ₂ , LiSPh	Ar	OTs	3	TL 35 5189 (1994)

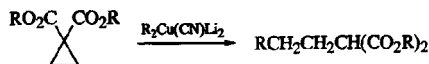
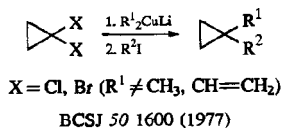


NaO ₂ CCF ₃ , CuI (R' = Ar; R = CF ₃)	CL 1719 (1981); 135 (1982)
RMgX, cat CuX (X = Br, CN)	JOC 52 3847 (1987) (heterocycles)
ArMgX, cat CuBr, HMPA	JOC 57 5243 (1992)
ArMgX, cat CuI	JOC 57 4074 (1992); 58 7149 (1993); 59 878, 4495 (1994) (all R' = ArCH ₂)
RMgX, CuBr·SMe ₂	JOC 55 3947 (1990)
RMgI, CuI	JACS 110 1626 (1988)
RMgX, cat CuCN, LiCl	TL 31 2295 (1990)
H ₂ C=CHCH ₂ MgCl, CuI	TL 28 2083 (1987)
RMnCl (R = 1°, 2°, 3° alkyl; aryl), cat Li ₂ CuCl ₄	SL 45 (1993)
CF ₃ Cu	Syn 932 (1980) JACS 108 832 (1986); 111 8502 (1989) TL 30 2133 (1989) JOC 58 2637 (1993)
C ₆ F ₅ CF ₂ CF ₂ Cu	JACS 114 4402 (1992)

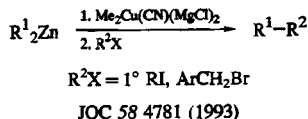
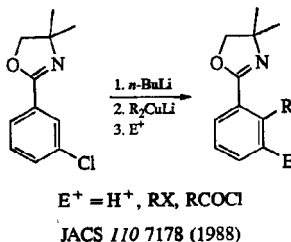
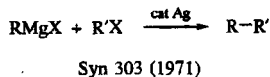
ArCu	TL 3307 (1968); 34 2279 (1993) JACS 90 2186 (1968); 102 790 (1980) Org Syn 59 122 (1980) JOC 52 547 (1987); 60 2361 (1995)
R ₂ CuLi	JACS 89 3911 (1967); 90 5615 (1968); 91 4871 (1969); 94 2520 (1972); 95 7777, 7783 (1973); 104 4696 (1982); 48 546 (1983); 113 631 (1991) JOC 39 400 (1974); 44 2705 (1979); 50 127 (1985); 52 4554 (1987); 54 5831 (1989) (X = OTs); 55 4417 (1990) (X = OTs) TL 683 (1974); 23 415 (1982); 24 3717 (1983); 27 4273 (1986); 28 3135 (1987); 31 5717 (1990); 33 4893 (1992) Syn 752 (1982) JOMC 251 133 (1983)
R ₂ CuMgX	JOC 57 3631 (1992)
R ₃ CuLi ₂	JOC 42 2805 (1977)
Me ₃ Cu ₂ Li, Me ₃ CuLi ₂ or Me ₃ Cu ₃ Li ₂	JOC 42 2805 (1977)
(RCuC≡CCMe ₂ OMe)Li	JOC 43 3418 (1978)
RCu(CN)Li	CC 88 (1973) JOMC 251 133 (1983)
ArCu(CN)Li	JACS 107 2712 (1985)
R ₂ Cu(CN)Li ₂	JACS 103 7672 (1981); 104 4696 (1982) JOC 48 3334 (1983); 49 3928 (1984); 54 5831 (1989) (X = OTs); 58 2181 (1993) (X = OTs)
ThCuR(CN)Li ₂	JOMC 285 437 (1985) TL 28 945 (1987)
[CH ₃ SOCH ₂ Cu(CN)R]Li ₂	JOC 52 1885 (1987)
R ₂ Cu(SCN)Li ₂	JOC 48 546 (1983) TL 28 2977 (1987)
RCu(NC ₂)Li	JACS 104 5824 (1982)
 NCuR(CN)Li ₂ (X = CH, N)	TL 33 1041 (1992)
RCu(PPh ₂)Li	JACS 104 5824 (1982)
[RCuP(<i>i</i> -Bu) ₂]Li	JACS 110 7226 (1988)
RCu(O- <i>i</i> -Bu)Li	TL 1815 (1973)



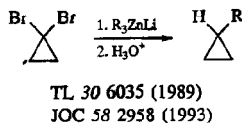
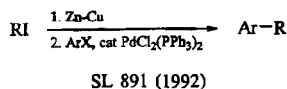
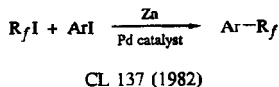
JACS 99 5816 (1977)
BCSJ 52 3632 (1979)

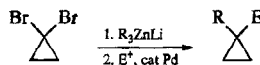


See page 1724, Section 2.

**2.24. Organosilver Reagents****2.25. Organozinc Reagents**

See also page 113, Section 2.15.

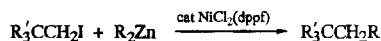




$\text{E}^+ = \text{ArX}, \text{C}=\text{C}-\text{X}, \text{RCOCl}, \text{ClCO}_2\text{R}$

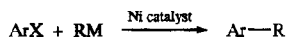
TL 30 6039 (1989)

JOC 58 2958 (1993)



$\text{R} = \text{Me}, \text{Ar}$

JOC 58 4866 (1993)



X

halogen

RM

$n\text{-BuZnCl}$

RZnX ($\text{R} = \text{benzylic}$)

ArZnX

Et_2Zn

RZnX ($\text{R} = \text{Me}, \text{Ar}$)

ArZnX

Bull Acad Sci USSR, Div Chem
Sci 620 (1986)

JOC 42 1821 (1977)

JOC 42 1821 (1977); 58 6692
(1993); 60 6658 (1995)

JACS 111 8055 (1989)

TL 31 4653 (1990); 35 2705
(1994)

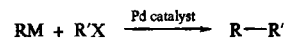
JACS 114 5269 (1992)

JOC 60 6895 (1995)

SL 349 (1994)

OMs

OTf



RM

1°RZnX

R'X

ArX

Het-X

ArX

ArX

ArO_3SR_f

Het-X

2°RZnX

PhCH_2ZnX

TL 24 3823 (1983); 34 5333
(1993); 35 1177 (1994)

Bull Acad Sci USSR, Div Chem
Sci 620 (1986)

JOC 55 5406 (1990); 60 8341
(1995)

TL 36 1945 (1995)

JACS 106 158 (1984)

JOC 42 1821 (1977)
TL 21 845 (1980); 34 5333
(1993)

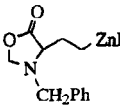
TL 28 2387 (1987)

TL 36 1945 (1995)

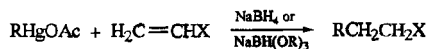
$\text{EtO}_2\text{C}(\text{CH}_2)_n\text{ZnX}$ ($n = 2, 3$)

ArX , allylic halide, vinylic
halide or triflate

See page 1724, Section 2.

$RM + R'X \xrightarrow{\text{Pd catalyst}} R-R'$		(continued)
<u>RM</u>	<u>R'X</u>	
$RO_2CCH(NHBoc)CH_2ZnI$	ArI	See page 1724, Section 2.
	ArX	See page 1724, Section 2.
$NC(CH_2)_3ZnX$	ArX	See page 1801, Section 6.
ArZnX	ArCH ₂ X ArX	JOC 60 6224 (1995) JOC 42 1821 (1977); 56 1445 (1991); 60 1856 (1995) TL 21 845 (1980); 22 5319 (1981); 34 5333, 5955 (1993) Org Syn 66 67 (1988) JACS 113 4576, 5775 (1991); 114 3983 (1992) SL 425 (1993); 347 (1994) Org Syn Coll Vol 8 430 (1993) TL 35 1909 (1994) SL 347 (1994) JOC 56 3493 (1991) JOC 53 386 (1988); 60 5255 (1995) TL 32 5919 (1991); 36 563 (1995) SL 425 (1993)
	(OC) ₃ Cr·ArX ArOTf ArOSO ₂ F Het-X	
(OC) ₃ Cr·ArZnX	Het-X	TL 28 2645 (1987)
Het-ZnX	ArX	Syn 51 (1987) TL 28 2645, 5213 (1987); 33 5373 (1992); 34 2437 (1993); 35 8329 (1994) SL 425 (1993) JACS 117 11680 (1995) JOC 60 6658, 8305 (1995) SL 47 (1990) TL 29 5013 (1988); 34 5005 (1993); 35 793, 7123 (1994); 36 7085 (1995) JACS 115 8716 (1993) JOC 60 1484, 2082 (1995)
	ArOTf Het-X	

2.26. Organomercury Reagents



X

Cl

Ber 112 3766 (1979)

Ar

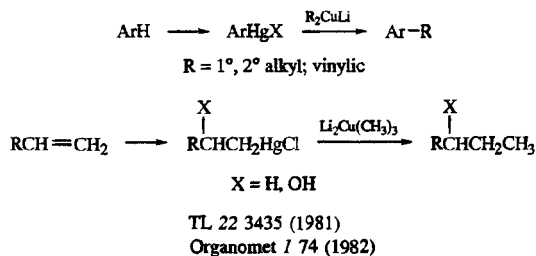
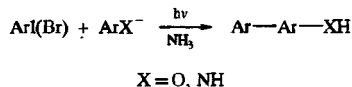
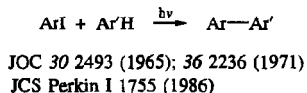
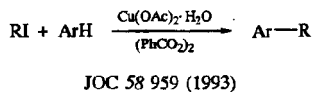
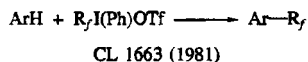
Angew Int 16 178 (1977); 18 154 (1979)

COR

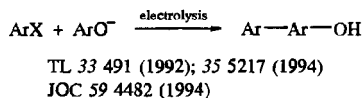
See page 1615, Section 21.

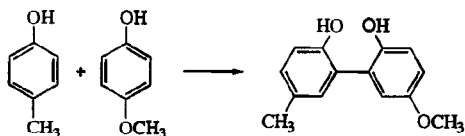
CO₂R, CO₂COR, CONR₂, CONRCOR, CN

See page 1809, Section 6.

**2.27. Miscellaneous Reagents**

TL 28 4653 (1987); 29 1289, 1705, 3429 (1988); 32 3487 (1991)
JOC 56 580, 2518 (1991); 58 2593 (1993)

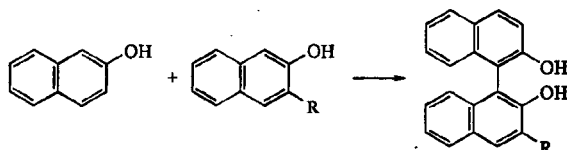


AlCl₃, DDQ

JOC 58 7271 (1993)

AlCl₃, FeCl₃

Tetr 48 9483 (1992)

NaOMe / CuCl₂

Tetr 48 9503, 9517 (1992)

CuCl(OMe)

Tetr 48 9503, 9517 (1992)

CuCl₂·4H₂O, *t*-BuNH₂

TL 31 413 (1990)

Org Prep Proc Int 23 200 (1991)

Tetr 48 9503, 9517 (1992)

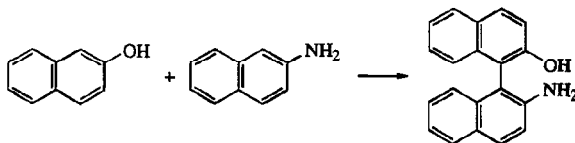
JOC 59 2156 (1994)

CuCl₂·4H₂O, sparteine (enantioselective)

JOC 58 4534 (1993)

Cu(NO₃)₂·3H₂O, PhCH(NH₂)CH₂Ph
(enantioselective)

CC 168 (1987)

CuCl₂·4H₂O, PhCH₂NH₂

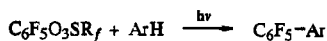
SL 231 (1991)

CuCl₂·4H₂O, PhCH(NH₂)CH₃
(enantioselective)

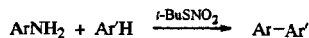
JOC 57 1917 (1992); 58 4534 (1993)

CuCl₂·4H₂O, *t*-BuNH₂

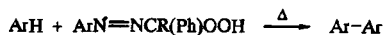
JOC 59 2156 (1994)



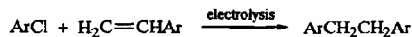
JOC 58 2599 (1993)



BCSJ 53 2023 (1980)

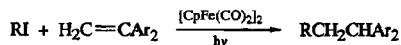


TL 30 963 (1989)

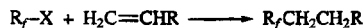


TL 29 639 (1988)

JOC 56 586 (1991)



TL 30 2907 (1989)



X

Reagents

Cl

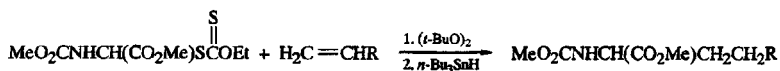
 $(\text{NH}_4)_2\text{S}_2\text{O}_8$, $\text{NaO}_2\text{CH}\cdot 2\text{H}_2\text{O}$

JOC 56 6348 (1991)

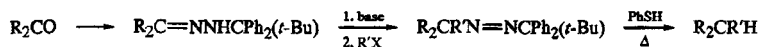
I

Zn, cat YbCl_3

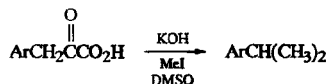
TL 34 1321 (1993)



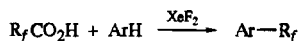
JOC 59 3721 (1994)



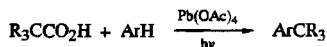
CC 176 (1986)



TL 35 4509 (1994)

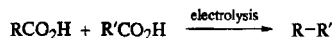


JOC 53 4582 (1988); 58 6922 (1993)



JACS 111 8943 (1989)

JOC 59 2986 (1994); 60 5303 (1995)



"Organic Electrochemistry," Ed. M. M. Baizer, M. Dekker, New York (1973), p 469

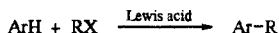
"Techniques of Chemistry," Ed. N. L. Weinberg, J. Wiley, New York (1974), Vol 5, Part 1, p 793

Angew Int 20 911 (1981)

Ann 1532 (1982)

3. FRIEDEL-CRAFTS AND RELATED ALKYLATION REACTIONS

See also page 125, Section 2.27.



Reviews:

Org Rxs 3 1 (1946)

Quart Rev 8 355 (1954)

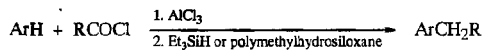
Ind Eng Chem 47 1926 (1955); 48 1670 (1956)

"Friedel-Crafts and Related Reactions," Ed. G. A. Olah, Interscience, New York (1964), Vol 2

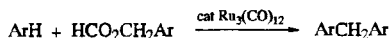
G. A. Olah, "Friedel-Crafts Chemistry," Wiley-Interscience, New York (1973)

R. M. Roberts, A. A. Khalaf, "Friedel-Crafts Alkylation Chemistry," Marcel Dekker, New York (1984)

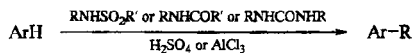
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.8, p 293



JCS Perkin I 1705 (1989)



TL 30 4137 (1989)



TL 35 2913 (1994)



HOAc

Org Syn Coll Vol 4 47 (1963)

HF

IACS 72 5232 (1951)

HBF₄·OMe₂

TL 30 3581 (1989) (intramolecular)

P₂O₅

JCS 2520 (1932) (intramolecular)

AlCl₃

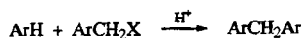
JACS 60 1421 (1938)

K10-montmorillonite

TL 34 1197 (1993)

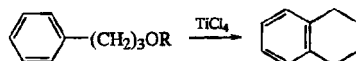
cation exchanged montmorillonite

JOC 59 5901 (1994)

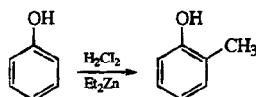


X = Cl, OH

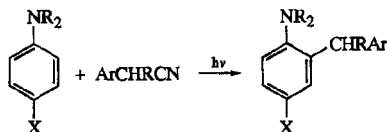
TL 34 529, 533 (1993)



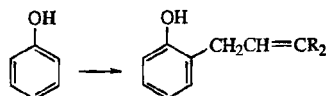
TL 30 5741 (1989)



TL 30 5215 (1989)

X = OR, NR₂

TL 31 4969 (1990)

NaH / R₂C=CHCH₂X, toluene

JCS Perkin I 1601 (1982)

KOH / R₂C=CHCH₂XTL 23 4567 (1982) (*m*-diphenol)NaOMe / R₂C=CHCH₂X

Ind J Chem 7 1072 (1969)

JOC 39 2215 (1974)

K / ZnCl₂ / R₂C=CHCH₂X

Syn 310 (1981)

Al₂O₃, R₂C=CHCH₂X

JOC 51 4481 (1986)

Ag₂O, R₂C=CHCH₂XTetr 28 4395 (1972) (*m*-diphenol)cat Cu, cat Cu(ClO₄)₂, H₂C=CHCH₂Cl

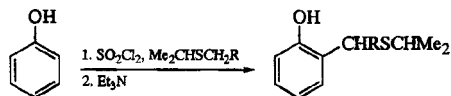
TL 36 8509 (1995)

H₂C=CHC(CH₃)=CH₂, Me₃SiCl, NaI

TL 25 5581 (1984)

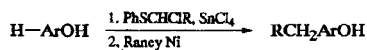
H₂C=CHC(CH₃)=CH₂, TsOH, NaI

TL 25 5581 (1984)

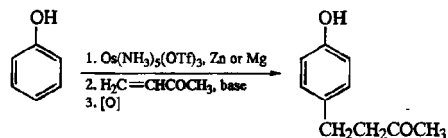


JACS 100 7611 (1978)

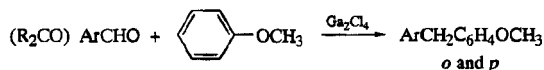
JOC 52 5495 (1987)



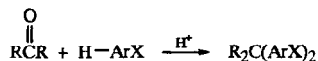
Syn 937 (1982)



JACS 116 6581 (1994)

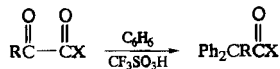


TL 33 6351 (1992)

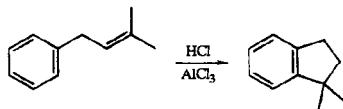
 $\text{X} = \text{OH}, \text{NR}_2$

JACS 114 5303 (1992)

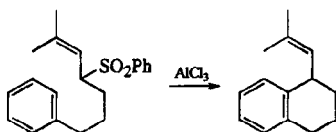
JOC 59 2506 (1994)

 $\text{X} = \text{R}, \text{Ph}, \text{OR}$

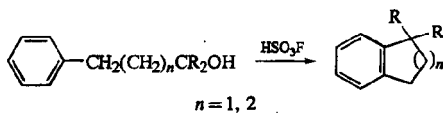
TL 36 5749 (1995)



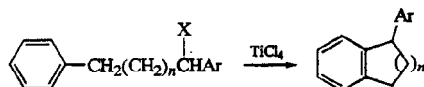
Bull Soc Chim Belg 90 847 (1981)



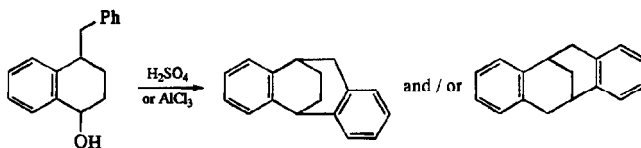
IACS 106 7260 (1984)

 $n = 1, 2$

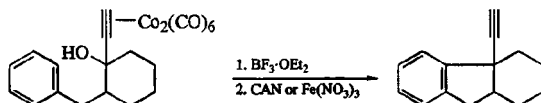
IOC 55 1338 (1990)

 $\text{X} = \text{Br}, \text{OH}, \text{OR}; n = 1, 2$

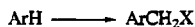
IOC 56 2853 (1991)



IOC 56 2998 (1991)



TL 31 6277 (1990); 35 8755 (1994)

 $\text{X} = \text{Cl}, \text{Br}, \text{I}$

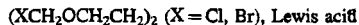
Reviews:

Org Rxs 1 63 (1942)

"Friedel-Crafts and Related Reactions," Vol 2, pp 659-784



IOC 41 1627 (1976)



Syn 560 (1974)

IOC 41 1627 (1976)

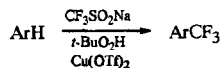
Org Prep Proc Int 14 3 (1982)

H₂CO, HCl, ZnCl₂, HOAc

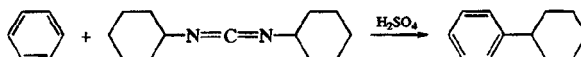
JACS 75 6292 (1953)

H₂CO, HBr, HOAc

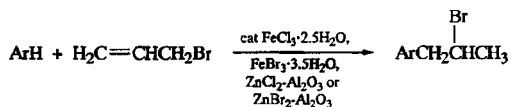
JOC 47 578 (1982); 52 3200 (1987)



TL 32 7525 (1991)



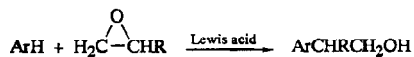
TL 35 903 (1994)



JOC USSR 18 115 (1982)



TL 29 1729 (1988)

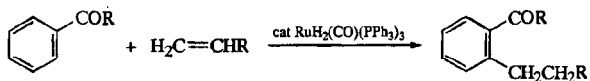


JCS 5404 (1964) (intramolecular)

Tetr 25 1807 (1969)

JOC 48 2449, 4572 (1983); 52 425 (1987) (all intramolecular)

TL 31, 7031 (1990)



Nature 366 529 (1993)

4. RING-FORMING REACTIONS

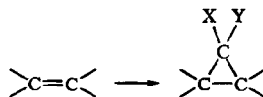
For a review of radical cyclizations, see *Org Rxns* 48 301 (1996).
See also page 1329, Section 6.

1. Three-Membered Rings

Reviews:

Houben-Weyl, Vol IV/3 (1971)

Israel J Chem 22 45 (1982) (using P ylids)



Reviews:

Syn 77 (1978) (synthesis of spiro compounds)

Tetr 36 2531 (1980) (α -heterosubstituted organometallics)

Acct Chem Res 13 58 (1980) (carbenes); 19 348 (1986) (metal carbenes)

Chem Rev 86 919 (1986) (metal carbenes)

Rec Trav Chim Pays Bas 110 305 (1991) (chiral catalysts)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),

Vol 4, Part 4.8, p 1031 (ketocarbenes)

"Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 3 (enantioselective synthesis)

SL 1197 (1995) (iodomethylzinc reagents and allylic alcohols)

CXY

Reagent(s)

CH₂

CH₂I₂, hv

JACS 100 655 (1978)

Tetr 37 3229 (1981)

CH₂I₂, MeLi

TL 29 6983 (1988)

CH₂I₂, R₃Al (R = Me, Et, *i*-Bu)

JOC 50 4412 (1985); 56 2202 (1991); 58 3589 (1993)




CXYReagent(s)CH₂ (*continued*)


- CC 157 (1987)
 TL 29 6979 (1988); 35 6453 (1994)
 Org Syn Coll Vol 8 321 (1993)
 JACS 98 2676 (1976); 101 2139 (1979)
- CH₂I₂, Cu
 CC 1460 (1987)
 JOC 59 2671 (1994)
 TL 23 2729 (1982)
 Org Prep Proc Int 16 25 (1984)
 JOC 59 2671 (1994)
- CH₂I₂, Cu, ultrasound
 JACS 80 5323 (1958); 81 4256 (1959); 85 468 (1963); 91 6892 (1969); 107 4984, 8256 (chiral) (1985); 108 3443 (1986)
- CH₂I₂, Zn
 JOC 24 1825 (1959); 33 1767, 2141 (1968); 51 2721 (1986) (diastereoselective); 52 3000 (1987) (diastereoselective); 53 5576 (1988); 54 250, 4951 (diastereoselective) (1989); 55 2045, 2055 (1990); 57 1114 (1992); 60 2474 (1995)
- CH₂I₂, Zn, cat Me₃SiCl
 Org Rxs 20 1 (1973) (review)
 Org Syn Coll Vol 5 855 (1973)
 J Chem Res (S) 179 (1978)
 TL 29 5775 (1988)
- CH₂I₂, Zn-Cu
 Syn 549 (1972)
 JACS 104 4290 (1982)
 TL 28 1865 (1987)
 JOC 52 603 (1987)
- CH₂I₂, Zn-Ag
 TL 23 259 (1982)
 JACS 109 3025 (1987)
- CH₂I₂, EtZnI
 TL 3353 (1966); 29 5775 (1988); 30 3807 (1989); 32 7219 (1991); 34 7157, 7291 (1993); 35 513 (1994); 36 357, 6831, 7221 (1995)
 Tetr 24 53 (1968)
- CH₂I₂, Et₂Zn
 JACS 106 3869, 6006 (1984); 107 8254 (1985) (chiral); 108 6343 (1986); 109 7553 (1987); 113 723, 5337, 8166 (chiral) (1991); 117 12721 (1995)
 JOC 52 3603 (1987); 56 2202, 6974 (1991); 57 5438 (1992); 59 97 (1994); 60 564, 2474, 2966 (1995)
 SL 410 (1992)

CH_2I_2 , Et_2Zn , ZnCl_2	TL 29 6979 (1988)
CH_2I_2 , Et_2Zn / TiCl_4	JACS 117 11367 (1995) (allylic alcohols)
CH_2I_2 , Et_2Zn / chiral Ti (enantioselective)	JACS 117 11367 (1995)
CH_2I_2 , Et_2Zn , chiral disulfonamide (enantioselective)	TL 33 2575 (1992); 35 7045 (1994); 36 2215, 2219 (1995)
CH_2I_2 , Et_2Zn , chiral dioxaborolane (enantioselective)	TL 35 9181 (1994); 36 1189, 5495, 8231 (1995) JACS 117 5612 (1995) (all allylic alcohols)
Et_2Zn , $\text{Me}_2\text{NCHMeCHPhOH}$ / $(\text{ICH}_2)_2\text{Zn}$ (enantioselective)	SL 229 (1992) (allylic alcohols)
$\text{Zn}(\text{CH}_2\text{I})_2$, chiral dioxaborolane (enantioselective)	JACS 116 2651 (1994) JOC 60 1081 (1995) (both allylic alcohols)
ClCH_2I , Et_2Zn	JOC 56 6974 (1991); 60 2474, 5236 (1995) TL 34 7157 (1993); 35 5405 (1994) JACS 117 12721 (1995)
ClCH_2I , Sm-HgCl_2	JOC 54 3525 (1989); 56 4167 (1991) (both allylic alcohols) TL 32 2343 (1991); 34 6233 (1993)
CH_2I_2 , Sm or $\text{Sm}(\text{Hg})$	JOC 52 3942 (1987); 54 3525 (1989); 57 798 (1992) (all allylic alcohols); 58 5037 (1993) (allenic alcohols to <div data-bbox="732 853 939 920" data-label="Chemical-Block"> </div>); 60 2474 (1995) (allylic alcohols)
CH_2Br_2 , CoCl_2 or NiBr_2 , Zn , NaI	JACS 116 8526 (1994) (allenic alcohols) CL 395 (1981)
CH_2Br_2 , cat $\text{Ni}(\text{COD})_2$, NaI	CL 761 (1979)
CH_2Br_2 ; cat $\text{Ni}(\text{PPh}_3)_4$; NaI , ZnX_2 ($\text{X} = \text{Cl}$, Br or I) or AlCl_3	CL 761 (1979)
CH_2Br_2 , Zn , CuCl , ultrasound	JOC 50 4640 (1985)
CH_2X_2 ($\text{X} = \text{Br}$, I), Zn , cat CuCl , cat AcCl	JOC 55 2491 (1990); 56 2202 (1991)
CH_2X_2 ($\text{X} = \text{Br}$, I), Zn , cat CuCl , cat TiCl_4	JOC 54 2388 (1989)
CH_2XY ($\text{X}, \text{Y} = \text{Cl}$, Br ; Br_2 ; I_2), electrolysis	JOC 56 3255 (1991)
$\text{CH}_2\text{N}_2/\Delta$ or hv	TL 23 2103 (1982); 30 3101, 5281 (1989); 35 5945 (1994) JOC 57 1074 (1992)

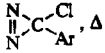
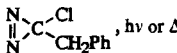
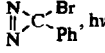


CXY	Reagent(s)	
CH ₂ (continued)	CH ₂ N ₂ , cat Pd(OAc) ₂	TL 1465 (1972); 629 (1975); 23 502 (1982); 28 4547 (1987); 30 4815 (1989); 32 5625 (1991) Syn 636 (1975); 714 (1981) JOC 51 4836 (1986); 55 1559 (1990); 56 4167, 6176 (1991); 59 4087 (1994); 60 2635, 3409 (1995)
	CH ₂ N ₂ , CuBr, cat Cu(OTs) ₂ ·2H ₂ O	Helv 59 1953 (1976)
	CH ₂ N ₂ , cat CuOTf·0.5C ₆ H ₆	JACS 95 3300 (1973); 107 996 (1985)
	CH ₂ N ₂ , cat Cu(OTf) ₂	JACS 95 3300 (1973)
	[CpFe(CO) ₂ CH ₂ ⁺ SMe ₂] ⁺ BF ₄ ⁻	JACS 101 6473 (1979); 109 3739 (1987) JOC 50 5898 (1985); 54 2467 (1989) TL 34 2007 (1993)
	[Me ₃ C ₃ Fe(CO) ₂ CH ₂ ⁺ SMe ₂] ⁺ BF ₄ ⁻	JOC 54 2467 (1989)
	$\bar{\text{C}}\text{H}_2\text{SMe}_2$ (on Michael acceptor)	TL 661 (1962) Ber 96 1881 (1963) JOC 29 3277 (1964); 33 3849 (1968); 34 3324 (1969); 37 2354 (1972); 53 2706 (1988) Ind J Chem B 19 563 (1980) SL 271 (1991)
	$\bar{\text{C}}\text{H}_2\text{SPh}_2$, cat Cu(<i>n</i> -C ₅ H ₁₁ CAc ₂) ₂	
	$\bar{\text{C}}\text{H}_2\text{SOMe}_2$ (on Michael acceptor)	JACS 84 3822 (1962); 87 1353 (1965); 106 5335 (1984); 107 4984 (1985); 110 7245 (1988) Z Naturforsch B 18 976 (1963) JOC 31 3467 (1966); 43 2839 (1978); 50 5898 (1985); 54 145 (1989); 55 3004 (1990); 57 5979 (1992); 60 2968, 3586 (1995) JCS C 2495 (1967) Angew Int 12 845 (1973) BSCF 888 (1974) TL 28 3201 (1987); 29 2111 (1988); 32 1275 (1991); 33 1701 (1992); 34 2007 (1993) SL 857 (1995)
	$\bar{\text{C}}\text{H}_2\text{SOCH}_3$ (on Michael acceptor) NR ₂	JOC 38 1793 (1973) JACS 110 3601 (1988)
	$\bar{\text{C}}\text{H}_2\text{SOPh}$ (on Michael acceptor) NEt ₂	JACS 113 8796 (1991)

	$t\text{-BuSO}_2\text{CH}_2\text{Li}$, cat $\text{Ni}(\text{acac})_2$	SL 56 (1991)
CH_2 , CHR, CR_2	$\begin{array}{c} \text{O} \\ \parallel \\ \text{Ar}^+\text{S}^-\text{CR}_2 \\ \\ \text{NMe}_2 \end{array}$	JACS 90 6852 (1968); 95 7418, 7692 (1973) Acct Chem Res 6 341 (1973)
CH_2 , CR_2 , CHCO_2R	R_2CN_2 , cat $\text{Cu}(\text{II})$	Tetr 24 3655 (1968) Can J Chem 47 1242 (1969)
CHR (R = H, Me)	RCHLi , $\text{R}'_3\text{Al}$	JOC 50 4412 (1985)
CHR (R = H, Me, Ph)	RCHLi , Et_2Zn	Tetr 25 2647 (1969); 27 1799 (1971) JOC 42 3031 (1977); 47 1615, 2426 (1982); 57 2007 (1992) TL 33 367 (1992)
CHCH_3	CH_3CHN_2 , $h\nu$ CH_3CHN_2 , cat CuCl CH_3CHLi , Zn, CuCl CH_3CHLi , Et_2Zn $\text{Ph}_2\text{SCH}^-\text{Me}$ (on Michael acceptor) $\text{CpFe}(\text{CO})_2\text{CH}(\text{CH}_3)\text{SPh}$, MeSO_2F or $(\text{Me}_3\text{O})\text{BF}_4$ $\text{CpFe}(\text{CO})(\text{PR}_3)=\text{CHCH}_3^+$	JACS 112 284 (1990) JOC 57 1074 (1992) TL 29 4835 (1988) JOC 47 1615, 2426 (1982) JACS 107 4230 (1985) JACS 117 5235 (1995) JOC 57 6265 (1992) JACS 103 1862 (1981) JOMC 285 231 (1985) JACS 113 927 (1991)
CHR	RCHN_2 RCHN_2 , CuI RCHN_2 , cat chiral $\text{CuOTf}(\text{bis-oxazoline})$ (enantioselective) $t\text{-BuSO}_2\text{CHRLi}$, cat $\text{Ni}(\text{acac})_2$ $\text{CpFe}(\text{CO})_2\text{CHRSPh}$, $(\text{Me}_3\text{O})\text{BF}_4$	JOC 53 4682 (1988) CL 863 (1982) (intramolecular) TL 36 8745 (1995) SL 269 (1991) JOC 50 5898 (1985) (intramolecular)
CHAr	$\text{ArCH}_2\text{Cl}(\text{Br})$, LiTMP PhCHX_2 (X = Cl, Br), electrolysis ArCHN_2 , ZnX_2 (X = Cl, Br, I) PhCHN_2 , cat $[\text{CpFe}(\text{CO})_2(\text{THF})]\text{BF}_4$ $\text{ArCH}(\text{OSiMe}_3)\text{Fe}(\text{CO})_2\text{Cp}$, Me_3SiOTf ArCHBrSiMe_3 , CsF Ph_2SCHPh (on Michael acceptor) $\text{PhCH}(\text{SeMe})\text{Li}$	JACS 95 581 (1973) Org Syn Coll Vol 6 571 (1988) JOC 56 1747 (1991) JOC 56 3255 (1991) JOC 34 25 (1969) TL 35 7561 (1994) TL 36 5113 (1995) JOC 56 3908 (1991) JOC 57 6265 (1992) SL 509 (1990)
CHCF_3	CF_3CHN_2 , $h\nu$	JCS 1881 (1964)

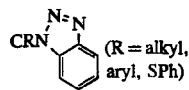
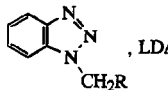
<u>CXY</u>	<u>Reagent(s)</u>	
CHCH(OMe) ₂	N ₂ CHCH(OMe) ₂ , Δ	TL 23 503 (1982)
	N ₂ CHCH(OMe) ₂ , hv	TL 21 2239 (1980)
CHCH=CH ₂	ClCH=CHCH ₂ Cl, Cu, <i>t</i> -BuNC	SL 913 (1994)
CHCH=C(CH ₃) ₂	BrCH ₂ CH=C(CH ₃) ₂ , LiTMP	SL 647 (1991)
	PhSO ₂ CH ₂ CH=C(CH ₃) ₂ , KO- <i>t</i> -Bu (on Michael acceptor)	BSCF 985 (1967)
	NO ₂ CH(K)CH=C(CH ₃) ₂ (on Michael acceptor)	JOC 50 2806 (1985)
CHR, (R = vinylic)	RCH(K)NO ₂ (R = vinylic, on Michael acceptor)	JOC 50 2806 (1985)
	Ph ₂ S ⁺ CHCH=CH ₂ (on Michael acceptor)	JOC 57 6265 (1992)
CRCH=C(OR') ₂ (R = H, Et, Ph, SiMe ₃)		TL 34 7429 (1993) SL 589 (1993)
CHCH=CHP(=O)(Me) ₂ 	ClCH=CHCH ₂ P(=O)(Me) ₂  base (on Michael acceptor)	JACS 117 10393 (1995)
C(CH ₃) ₂	Ph ₂ S ⁺ C(CH ₃) ₂ (on Michael acceptor)	JACS 89 3912 (1967) TL 3915 (1976); 29 1083 (1988, 30 1745 (1989); 34 2695 (1993) JOC 57 6265 (1992)
	(<i>i</i> -Pr) ₂ SONTs, <i>n</i> -BuLi (on Michael acceptor)	TL 32 1275 (1991); 34 2695 (1993)
	Ph ₃ P=C(CH ₃) ₂ (on Michael acceptor)	TL 3911 (1976); 1847 (1978); 24 103 (1983); 29 1079 (1988); 34 2691, 2695, 5799 (1993) Angew Int 22 63 (1983) JOC 58 6292 (1993)
	(CH ₃) ₂ CN ₂ , hv (on Michael acceptor)	TL 30 1745 (1989) JOC 57 1074 (1992)
	(CH ₃) ₂ CBr ₂ , <i>n</i> -BuLi	Angew Int 20 863 (1981)
	(CH ₃) ₂ CBr ₂ , electrolysis	JOC 56 3255 (1991)
	(CH ₃) ₂ CH(K)NO ₂ , DMSO (on Michael acceptor)	JOC 50 2806 (1985); 56 1747 (1991)
C(CF ₃) ₂	N ₂ C(CF ₃) ₂ , Δ	JACS 88 3617 (1966)
CR ₂	R ₂ CH(K)NO ₂ , DMSO (on Michael acceptor)	JOC 50 2806 (1985)
	PhSeO ₂ CHR ₂ , KO- <i>t</i> -Bu (on Michael acceptor)	TL 29 3269 (1988)

	$\text{Ph}_3\text{P}=\text{CR}_2$ (on Michael acceptor)	TL 3911 (1976); 1847 (1978)
C(Ph)Me	Ph(Me)C(SeMe)Li	SL 509 (1990)
CPh_2	Ph_2CN_2 , hv	JOC 53 3298 (1988)
CHF	CHF_2 , hv CHF_2 , Et_2Zn	TL 1819 (1975) CC 1375 (1971) TL 33 3483, 3487 (1992)
CHCl	CH_2Cl_2 , $n\text{-BuLi}$ CH_2Cl_2 , $\text{NaN(SiMe}_3)_2$ HCCl_2I , Et_2Zn HCClBrI , Et_2Zn	JACS 82 5729 (1960) Can J Chem 59 621 (1981) Tetr 41 2643, 2653 (1985) JOC 55 4807 (1990) CC 1375 (1971) CC 1375 (1971)
CHBr	CH_2Br_2 , $\text{NaN(SiMe}_3)_2$ HCBBr_2I , Et_2Zn	Syn 201 (1972) TL 32 6105 (1991) JOC 57 2007 (1992); 59 4087 (1994) CC 1375 (1971)
CHI	HCl_3 , NaOH , hv	Org Syn Coll Vol 6 974 (1988)
CHX (X = Cl, Br)	XCHN_2	JACS 84 4350 (1962); 87 4270 (1965)
$\text{CHX (X = Cl, Br, I)}$	HCXI_2 , hv	JACS 90 5644 (1968) Org Syn 52 132 (1972) TL 32 6105 (1991)
$\text{CHX (X = F, Cl, Br, I)}$	HCXI_2 , Cu HCX_3 or HCXI_2 , Et_2Zn	Tetr 35 1919 (1979) CC 1375 (1971) (X = F, Cl, Br, I); 364 (1975) (X = Br) BCSJ 47 1500 (1974) (X = I) TL 32 6105 (1991) (X = I)
CF_2	F_2CBr_2 , $\text{LiAlH}_4\text{-TiCl}_4$ F_2Cl_2 , $\text{LiAlH}_4\text{-TiCl}_4$ F_2CBr_2 , Zn  $\text{N} \begin{array}{c} \text{F} \\ \text{C} \\ \text{F} \end{array}$, Δ or hv $\text{ClCF}_2\text{CO}_2\text{Na}$, Δ	JOC 55 589, 5420 (1990) JOC 55 5420 (1990) JOC 55 5420 (1990) JOC 35 678 (1970) JCS Perkin I 2203 (1982) JACS 87 758 (1965) JACS 85 1851 (1963)
CCl_2	H_2CCl_2 , CCl_4 , KOH , cat $n\text{-Bu}_4\text{NHSO}_4$ HCCl_3 , NaOH , ultrasound HCCl_3 , NaOH , phase transfer	TL 30 4697 (1989) JOC 47 1587 (1982) TL 4659 (1969); 1461 (1972); 27 893 (1986); 32 5733 (1991) Ann 744 42 (1971); 591 (1981) Tetr 28 175 (1972)

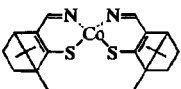
<u>CXY</u>	<u>Reagent(s)</u>	
CCl ₂ (<i>continued</i>)		Syn 682 (1977); 1004 (1981) JOC 44 447 (1979); 52 3579 (1987); 56 2040 (1991) J Chem Res (S) 354 (1982) JOC USSR 18 828 (1982) Org Syn Coll Vol 7 12 (1990) Steroids 39 371 (1982)
	HCCl ₃ , OH ⁻ , phase transfer, ultrasound	
	HCCl ₃ , NaOH, cat Me ₄ NX (X = Br, HSO ₄ , H ₂ O; on Michael acceptor)	JOC 58 6120 (1993)
	HCCl ₃ , KO- <i>t</i> -Bu	JACS 76 6162 (1954); 78 1437 (1956); 80 5274 (1958) Org Syn Coll Vol 6 87, 731 (1988)
	XCCl ₃ (X = Br, I), RLi (R = Me, <i>n</i> -Bu)	JACS 81 5009 (1959)
	CCl ₄ , LiAlH ₄ -TiCl ₄	JOC 55 589 (1990)
	Cl ₃ CCO ₂ Na, Δ	JACS 85 1851 (1963) JOC 29 1113 (1964); 53 4945 (1988); 59 1953 (1994)
	Cl ₃ CCO ₂ Na, R ₄ NBr, Δ	J Chem Res (S) 72 (1977) Helv 65 1191 (1982)
	Cl ₃ CCO ₂ Et, NaOR (R = Me, Et) or KO- <i>t</i> -Bu	JOC 24 1733 (1959); 40 2234 (1975) JACS 82 4085 (1960) Org Syn Coll Vol 5 874 (1973)
CBr ₂	HCBBr ₃ , NaOH, phase transfer	TL 1367 (1973) Syn 296 (1982) JOC 47 3211 (1982); 52 4732 (1987); 60 4666 (1995) JOC USSR 18 71 (1982) JACS 114 601 (1992)
	HCBBr ₃ , NaOH, <i>n</i> -Bu ₃ N	JACS 107 8066 (1985)
	HCBBr ₃ , KO- <i>t</i> -Bu	JOC 47 3211 (1982); 58 6497 (1993) JOC USSR 18 71 (1982) Org Syn Coll Vol 6 187 (1988); 7 200 (1990)
CX ₂ (X = Cl, Br)	HCCX ₃ , NaOH	TL 1749 (1965)
CXY (X, Y = F, Cl, Br, I)	PhHgCXYZ (Z = F, Cl, Br, I)	Acct Chem Res 5 65 (1972) Russ Chem Rev 46 941 (1977) R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer, New York (1985), Chpt 10 (all reviews)
CFCI	FCCL ₂ COCCL ₂ F, KO- <i>t</i> -Bu	JOC 28 2494 (1963)

	HCCl ₂ F, NaOH	TL 1749 (1965)
	HCCl ₂ F, NaOH, (PhCH ₂ NEt ₃)Cl	JOC 54 5618 (1989)
	HCCl ₂ F, KO- <i>t</i> -Bu	BSCF 455 (1985)
	Cl ₃ CF, LiAlH ₄ -TiCl ₄	TL 29 6749 (1988)
		JOC 55 589 (1990)
CFBr	HCBF ₂ F, NaOH, phase transfer	Ann 591 (1981)
CClCH ₃	CH ₃ CHCl ₂ , RLi	Syn 801 (1974); 58 (1982)
		Can J Chem 60 1933 (1982)
		Tetr 41 2643, 2653 (1985)
		JACS 108 1251 (1986)
		JOC 52 1475 (1987); 55 4807 (1990); 56 6176 (1991); 57 701 (1992)
	CH ₃ CHCl ₂ , NaN(SiMe ₃) ₂	Tetr 41 2653 (1985)
CCIR	RCHCl ₂ , <i>n</i> -BuLi	JOC 57 701 (1992)
CClCH=CH ₂	Cl ₂ CHCH=CH ₂ , LiTMP	Syn 425 (1979)
CClCCl=CCl ₂	tetrachlorocyclopropene, Δ	TL 23 3341 (1982)
CClAr	 , Δ	Org Syn 60 53 (1981)
		TL 25 901 (1984); 27 4395 (1986)
		JOC 53 4193 (1988)
		JACS 110 7143 (1988)
		Org Syn Coll Vol 7 203 (1990)
CClCH ₂ Ph	 , hv or Δ	JOC 52 4223 (1987)
CBrPh	 , hv	TL 4905 (1967)
CHMMe ₃ (M = Si, Sn)	ClCH ₂ MMe ₃ , LiTMP	TL 1677 (1978)
CHOR	ClCH ₂ OR, LiTMP	TL 3779 (1976)
		JOC 58 6851 (1993)
	ClCH ₂ OR, RLi	Angew 73 27, 765 (1961)
		Ber 96 2266 (1963); 97 636 (1964)
	Cl ₂ CHOR, MeLi	Ber 98 2221 (1965)
CROR	(CO) ₅ M=CROME (M = Cr, Mo; 1,3-dienes only)	JACS 113 8916 (1991)
	(CO) ₅ Mo=CROME (on Michael acceptor)	TL 31 2529 (1990)
	RC(OR)(N ₃) ₂ , hv	TL 31 4441 (1990)
	ROCR=NN(Na)Ts, hv	SL 119 (1992)
C(OMe)- 	(CO) ₅ Cr=C(OMe)-  (on Michael acceptor, 1,3-dienes)	TL 30 4771 (1989)
		JOC 56 286 (1990)

<u>CXY</u>	<u>Reagent(s)</u>	
$C(OR)CH=CH_2$ (R = Me, Et)	$H_2C=CHC(Li)(OR)-$ (benzotriazoly) (on Michael acceptor)	JOC 60 6, 7597 (1995)
$C(OMe)CH=CHR$	$RCH=CHC(OMe)=PPh_3$ (on Michael acceptor)	TL 34 7583 (1993)
	$(CO)_5Cr=C(OMe)CH=CHR$ (on Michael acceptor)	TL 29 2315 (1988)
$C(Ph)OMe$	$\begin{array}{c} N \\ \diagup \\ C-OMe \\ \diagdown \\ N \end{array} Ph$, hv or Δ	CC 432 (1982)
	$(CO)_5Mo=C(Ph)OMe$ (1,3-dienes)	JACS 109 4341 (1987)
	$(CO)_5Cr=C(Ph)OMe$	JACS 113 8916 (1991)
		TL 29 2315 (Michael acceptor), 2319 (Michael acceptor, 1,3-diene) (1988)
		JACS 113 8916 (1991) (1,3-dienes)
$C(CH_3)OSiMe_3$	$CH_3COSiMe_3$, hv	JACS 103 699 (1981)
$CCl(OPh)$	$\begin{array}{c} N \\ \diagup \\ C-Cl \\ \diagdown \\ N \end{array} OPh$, Δ	JOC 47 4177 (1982)
	$HCCL_2OPh$, NaOH, phase transfer	Angew Int 21 916 (1982)
$C(OMe)OPh$	$\begin{array}{c} N \\ \diagup \\ C-OMe \\ \diagdown \\ N \end{array} OPh$, Δ	JACS 109 3811 (1987)
$CR(O_2CR)$	$(CO)_5Cr=CR(O_2CR)$	JACS 112 5660 (1990)
$CHSPh$	$ClCH_2SPh$, NaOH, $(PhCH_2NEt_3)Cl$	TL 4247 (1975); 28 4797 (1980)
	$ClCH_2SPh$, NaH	Compt Rend C 275 283 (1972)
	$LiC(SPh)_3/sec-BuLi$ (enones)	JOC 54 4404 (1989)
$CHSAr$	$ClCH_2SAr$, KO- <i>t</i> -Bu	Angew 73 765 (1961)
		TL 165 (1962)
		Ber 97 1527 (1964)
		BCSJ 52 3434 (1979)
	$ClCH_2SAr$, <i>n</i> -BuLi	Angew 73 765 (1961)
		TL 165 (1962)
		Ber 97 1527 (1964)
$CCISPh$	Cl_2CHSPh , NaOH, $(PhCH_2NEt_3)Cl$	TL 4517 (1971)
	Cl_2CHSPh , KO- <i>t</i> -Bu	JACS 115 10754 (1993)
		Ber 99 806 (1966)
$C(SiMe_3)SPh$	$LiC(SPh)_2SiMe_3/CuOTf$ (on enone)	JOC 53 457 (1988)
$C(SPh)_2$	$LiC(SPh)_3/CuOTf$ (on enone)	JOC 53 457 (1988)

CHCH=CHSPh	LiCH(SPh)CH=CHSPh/ CuOTf (on enone)	JOC 53 457 (1988)
CHCH=C(SPh) ₂	LiCH(SPh)CH=C(SPh) ₂ / CuOTf (on enone)	JOC 53 457 (1988)
CHSO ₂ C ₆ H ₄ CH ₃ - <i>p</i>	<i>p</i> -CH ₃ C ₆ H ₄ SO ₂ CHN ₂ , cat Cu(acac) ₂	JOC 52 4760 (1987)
 (R = alkyl, aryl, SPh)	 , LDA	SL 213 (1993)
CRCHO	HCOCRN ₂ , cat Cu(II) (enantio- selective)	TL 31 6969 (1990) (intramolecular)
CHCOR	RCOCHN ₂ RCOCHN ₂ , hv, PhCOPh RCOCHN ₂ , cat Mo(CO) ₆ PhCOCHN ₂ , cat Mo(CO) ₆ or Mo ₂ (OAc) ₄ RCOCHN ₂ , cat Rh ₂ (OAc) ₄	Org Rxs 26 361 (1980) (intramolecular, review) JACS 90 2200 (1968) JOC 45 1538 (1980) JOC 47 4059 (1982) TL 27 2075 (1986) (intramolecular) JOC 51 3878 (1986) (intramolecular); 54 5126 (1989); 56 4494 (1991) (intramolecular); 57 441 (1992) (intramolecular); 60 3580 (1995) (intramolecular) JACS 109 5432 (1987); 112 260 (1990) (both intra- molecular) JACS 114 1874 (1992); 115 8669 (1993) (both intramolecular) SL 1121 (1995)
	RCOCHN ₂ , cat Rh ₂ (cap) ₄ (cap = caprolactam)	JACS 114 1874 (1992); 115 8669 (1993) (both intramolecular)
	RCOCHN ₂ , cat Rh ₂ (O ₂ CR) ₂ (-ArPR ₂) ₂ RCOCHN ₂ cat Ni(acac) ₂ , hv	Ind J Chem B 20 911 (1981) (intramolecular)
	RCOCHN ₂ , cat Pd(OAc) ₂	Tetr 36 3269 (1980) TL 23 2411 (1982)
	RCOCHN ₂ , cat Cu	JACS 103 1808, 1813 (1981) (both intramolecular)
	RCOCHN ₂ , cat Cu-bronze or CuSO ₄	Tetr 28 4653 (1972) (intramolecular)
	RCOCHN ₂ , cat Cu, cat CuSO ₄	Tetr 26 2815 (1970) JACS 109 3147 (1987) JOC 52 4634 (1987) (all intramolecular)
	RCOCHN ₂ , cat CuSO ₄	Israel J Chem 10 375 (1972) (intramolecular)

<u>CXY</u>	<u>Reagent(s)</u>	
CHCOR (continued)	RCOCHN ₂ , cat Cu(acac) ₂	JOC 45 5020 (1980) (intramolecular) TL 29 611 (1988) (intramolecular); 36 8213 (1995)
	RCOCHN ₂ , cat CuSO ₄ , cat Cu(acac) ₂	JOC 47 1522 (1982); 52 4641 (1987)
	RCOCHN ₂ , cat chiral semicorrin Cu (enantioselective)	SL 491 (1995) (intramolecular)
	RCOCHN ₂ , cat Cu(II) (enantioselective)	TL 31 6969 (1990) (intramolecular)
	RCOCH ⁺ SM ₂ (on Michael acceptor)	JACS 89 138 (1967) Ind J Chem B 20 168 (1981); 21 959 (1982) JOC 58 5853 (1993) TL 34 6567 (1993)
	RCOCH ₂ Cl, <i>n</i> -Bu ₃ SnN(Et)-CO ₂ Me (on enone)	
	H ₂ C=C(OSiR ₃)CHROAc, cat Pd ₂ (DBA) ₃ ·CHCl ₃ , cat PPh ₃	TL 31 615 (1990) (bicyclic alkenes)
	N ₂ CRCOR, hv, PhCOPh	JACS 90 2200 (1968)
	N ₂ CRCOR, cat CuSO ₄	TL 1363 (1972); 30 6577 (1989) (both intramolecular)
	N ₂ CRCOR, cat Cu(acac) ₂	JOC 45 5020 (1980) (intramolecular)
CRCOR	N ₂ CRCOR, cat Cu(II) bis(<i>N</i> - <i>n</i> -butylsalicylideneaminate)	JACS 106 6006 (1984) (intramolecular)
	N ₂ CRCOR, cat bis(<i>N</i> - <i>t</i> -butylsalicylaldiminato)Cu(II)	JOC 60 3580 (1995) (intramolecular)
CHCO ₂ H	Ph ₂ SC ⁺ HCO ₂ ⁻ (on Michael acceptor)	JOC 57 6265 (1992)
CHCO ₂ R	ClCH ₂ CO ₂ R, LDA (on Michael acceptor)	JOC 54 3800 (1989)
	ClCH ₂ CO ₂ R, NaH, DMSO (on Michael acceptor)	JACS 114 9401 (1992)
	ClCH ₂ CO ₂ R, <i>n</i> -Bu ₃ SnN(Et)-CO ₂ Me (on enone)	TL 34 6567 (1993)
	Ph ₂ SC ⁺ HCO ₂ R (on Michael acceptor)	JOC 57 6265 (1992)
	Ph ₂ SC ⁺ HCO ₂ R, cat Cu(acac) ₂	SL 271 (1991)
	Br ₂ CHCO ₂ Me, Cu	JACS 98 2676 (1976); 101 2139 (1979)
	N ₂ CHCO ₂ R, hv or Δ	Org Rxs 18 217 (1970) (review) Org Syn 50 94 (1970) Chem Rev 75 431 (1974) Org Syn Coll Vol 6 913 (1988)

N_2CHCO_2R , $(Ar_3N)SbCl_6$	JACS 108 4234 (1986); 117 5671 (1995)
N_2CHCO_2Et , cat $Mo(CO)_6$	JOC 45 1538 (1980)
N_2CHCO_2Et , cat $Mo(CO)_6$ or $Mo_2(OAc)_4$	JOC 47 4059 (1982)
N_2CHCO_2R , cat $CpFe(CO)_2(THF)BF_4$	TL 33 7755 (1992)
N_2CHCO_2R , cat Fe porphyrin	JACS 117 9194 (1995)
N_2CHCO_2R , cat chiral $RuCl_2[bis(oxazolinyl)pyridine](C_2H_4)$ (enantioselective)	JACS 116 2223 (1994)
N_2CHCO_2Et , cat $RuCl_2(PPh_3)_3$	TL 36 3519, 8419 (1995)
N_2CHCO_2Et , cat $RuH_3[Si(OEt)_3](PPh_3)_2$	TL 36 3519 (1995)
N_2CHCO_2Et , cat $Ru[Si(OEt)_3]_2(PPh_3)_2$	TL 36 3519 (1995)
N_2CHCO_2R , cat Ru-carborane	TL 33 2009 (1992)
N_2CHCO_2Et , cat Os porphyrin	JACS 115 2511 (1993)
N_2CHCO_2R , cat $OsCl_2(PPh_3)_3$	TL 36 8419 (1995)
N_2CHCO_2R , cat	SL 833 (1993)
	
(enantioselective)	
N_2CHCO_2R , cat chiral Co(III)-salen (enantioselective)	SL 825 (1995)
N_2CHCO_2Et , cat $Rh_6(CO)_{16}$	TL 22 1783 (1981); 23 2261 (1982)
	Syn 787 (1981)
N_2CHCO_2R , cat Rh(I) carboxylate polymer	TL 32 2731 (1991)
N_2CHCO_2R , cat $Rh_2(OAc)_4$	JOC 45 695 (1980); 54 3096 (1989)
	Syn 787 (1981)
	TL 23 2261 (1982); 28 833 (1987); 31 139, 4731 (1990)
	JACS 112 1906 (1990); 113 7388 (1991); 115 11370 (1993); 117 7281 (1995)
	(intramolecular)
	SL 151 (1993)
N_2CHCO_2R , cat $Rh_2(O_2CCF_3)_4$	TL 28 833 (1987)
	JACS 112 1906 (1990); 117 7281 (1995) (intramolecular)
N_2CHCO_2R , other $Rh_2(O_2CR)_4$	JACS 112 1906 (1990); 117 7281 (1995) (intramolecular)
N_2CHCO_2R , cat $Rh_2(NHCOCH_3)_4$	TL 28 833 (1987)
N_2CHCO_2R , cat $Rh_2(caprolactamate)$	JACS 112 1906 (1990)
	JACS 117 11021 (1995) (intramolecular)

CXY

CHCO₂R (*continued*)

Reagent(s)

N₂CHCO₂R, cat Rh₂[Me 2-pyrrolidone-5-carboxylate]₄ (enantioselective)

TL 31 6613 (1990); 33 6727 (1992) (intramolecular)
JACS 113 1423 (1991) (intramolecular); 115 1423 (1993) (inter- and intramolecular); 116 4493 (1994) (intramolecular); 117 5763, 7281, 11021 (1995) (all intramolecular)
SL 151 (1993)
JOC 60 941 (1995) (intramolecular)

N₂CHCO₂R, cat Rh₂[2-pyrrolidone-5-carboxylate]-polymer (enantioselective)

JOC 57 6103 (1992) (inter- and intramolecular)

N₂CHCO₂R, cat Rh₂[Me 1-(3-phenylpropanoyl)-imidazolidin-2-one-4-carboxylate]₄ (enantioselective)

TL 36 7579 (1995)

N₂CHCO₂R, cat Rh₂[4-methoxycarbonyl-2-oxoxazolidinyl]₄ (enantioselective)

TL 36 7579 (1995)
JACS 117 11021 (1995) (intramolecular)

N₂CHCO₂Et, cat Rh(III)-porphyrins

Tetr 38 2365 (1982)
JACS 115 1656 (1993)

N₂CHCO₂R, cat Rh(III)-tetraarylporphyrin

TL 21 3489 (1980); 32 2445 (1991) (chiral)

N₂CHCO₂Et, cat Pd(OAc)₂

TL 1465 (1972); 629 (1975); 29 1181 (1988); 30 4815 (1989)
JOC 45 695 (1980); 56 4167 (1991)

N₂CHCO₂Et, cat PdCl₂(PhCN)₂

SL 873 (1991)
TL 23 2261 (1982)

N₂CHCO₂Et, cat π -allyl-palladium chloride

JOC 52 5158 (1987)

N₂CHCO₂Et, cat Cu

JOC 38 2221 (1973); 57 1784 (1992); 60 829 (1995)

N₂CHCO₂R, cat Cu(I), cat bis(oxazoline) (enantioselective)

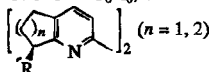
JACS 113 726 (1991)
TL 32 7373 (1991)

N₂CHCO₂R, cat Cu[bis(oxazoline)]₂ (enantioselective)

TL 31 6005 (1990)

N₂CHCO₂R, cat CuOTf·0.5C₆H₆, cat


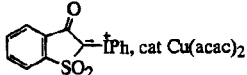
SL 575 (1992)
TL 34 2661 (1993)



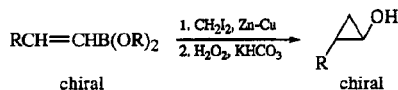
(enantioselective)
N₂CHCO₂R, cat CuOTf, cat chiral bipyridine (enantioselective)

SL 638 (1993)

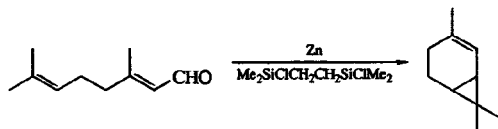
	N_2CHCO_2R , cat Cu semicorrin (enantioselective)	TL 30 2079 (1989)
	N_2CHCO_2R , cat bis[N-alkyl- salicylaldiminato]Cu (enantioselective)	Tetr 24 3655 (1968) TL 1707 (1975); 23 685 (1982); 30 2079 (1989) JACS 104 1362 (1982); 106 1421, 5312, 6364 (1984)
	N_2CHCO_2R , cat Cu(II) bis(salicylaldehyde- <i>l</i> - butylimine)	TL 25 3559 (1984); 31 4731 (1990); 32 5025 (1991) (all intramolecular) JACS 107 5574 (1985); 116 4493 (1994) (intramolecular)
	N_2CHCO_2R , cat Cu(acac) ₂	TL 27 2139 (1986) (intramolecular)
	N_2CHCO_2Et , cat CuCl-(<i>i</i> -PrO) ₃ P	TL 23 2261 (1982)
	N_2CHCO_2Et , cat CuI	JOC 50 2026 (1985)
	N_2CHCO_2Et , cat CuSO ₄	Can J Chem 60 2383 (1982) JACS 106 1421 (1984); 107 734 (1985); 110 3601 (1988) JOC 52 4898 (1987)
	N_2CHCO_2R , cat CuSO ₄	Israel J Chem 10 375 (1972) (intramolecular)
	N_2CHCO_2Et , cat CuOTf·0.5C ₆ H ₅	JACS 95 3300 (1973); 107 996 (1985)
	N_2CHCO_2Et , cat CuOTf or Cu(OTf) ₂ , cat bis(aziridine) (enantioselective)	TL 35 4631 (1994)
	N_2CHCO_2R , cat Cu(OTf) ₂	JACS 95 3300 (1973) JOC 45 695 (1980)
	N_2CHCO_2R , cat Cu(OTf) ₂ , cat diamine (enantioselective)	TL 35 7985 (1994)
CHCONHR	$N_2CHCONHR$, cat Rh amide (enantioselective)	JACS 117 5763 (1995) (intramolecular)
CHCONHAr	$N_2CHCONHAr$, cat Rh ₂ (O ₂ CR) ₄	JOC 51 5362 (1986)
CHCONR ₂	$N_2CHCONR_2$, cat Pd(OAc) ₂	TL 29 1181 (1988); 31 4049 (1990) (both intramolecular)
	$N_2CHCONR_2$; cat Rh ₂ (OAc) ₄ , Rh ₂ (O ₂ CCF ₃) ₄ or Rh ₂ (NHCOCH ₃) ₄	TL 28 833 (1987)
	$N_2CHCONR_2$, cat Rh ₂ [Me 2- pyrrolidone-5-carboxylate] ₄ (enantioselective)	JACS 117 5763 (1995) (intramolecular)
C(Cl)CO ₂ R	HCCL ₂ CO ₂ R, base (on Michael acceptor)	TL 31 7181 (1990)
C(NO ₂)CO ₂ R	$N_2C(NO_2)CO_2R$, cat Rh ₂ (OAc) ₄	JOC 54 3096 (1989)
CRCO ₂ R	RCHXCO ₂ R (X = Cl, Br), NaH or NaOMe	JACS 80 6568 (1958)
	N_2CRCO_2R , cat Rh ₂ (OAc) ₄	JACS 115 11370 (1993)

<u>CXY</u>	<u>Reagent(s)</u>	
	N_2CRCO_2R , cat Cu(II) (enantioselective)	TL 31 6969 (1990) (intramolecular)
$C(CF_3)CO_2R$	$N_2C(CF_3)CO_2R$, cat $Rh_2(OAc)_4$	JOC 55 3383 (1990)
$C(CH=CH_2)CO_2Et$	$CH_3CH=CHCO_2Et$, LDA (on Michael acceptor)	JOC 51 4746 (1986); 52 4397, 4641 (1987) TL 29 3283 (1988) JACS 111 6691 (1989)
$C(CH=CH_2)CO_2Me$	$H_2C=CHC(N_2)CO_2Me$, cat $Rh_2(O_2CR)_4$	TL 33 453 (1992)
$C(CR=CR_2)CO_2R$	$R_2C=CR(CN_2)CO_2R$, cat $Rh_2(O_2CR)_4$	JOC 56 723 (1991); 57 3186 (1992) TL 32 6509 (1991) (chiral); 34 7243 (1993) (chiral); 35 5373, 8939 (1994) JACS 115 9468 (1993) (chiral)
$C(COR)SO_2Ph$	$N_2C(COR)SO_2Ph$, cat $Rh_2(OAc)_4$	TL 28 3459 (1987) (intramolecular)
		TL 30 6673 (1989)
$C(COR)_2$	$N_2C(COR)_2$, hv, PhCOPh	JACS 106 6006 (1984) (intramolecular)
	$N_2C(COR)_2$, cat $Rh_2(OAc)_4$	JOC 53 2699 (1988)
$C(COR)CO_2R$	$N_2C(COR)CO_2R$, hv, PhCOPh	JACS 106 6006 (1984) (intramolecular)
	$N_2C(COR)CO_2R$, cat $Ru_3(CO)_{12}$	JOC 53 2984 (1988) (intramolecular)
	$N_2C(COR)CO_2R$, cat Rh(III) porphyrin	JOC 53 2984 (1988) TL 32 2339 (1991) (both intramolecular)
	$N_2C(COR)CO_2R$, cat $Rh_2(OAc)_4$	JOC 58 7751 (1993) TL 36 2385 (1996) (both intramolecular)
	$N_2C(COR)CO_2R$, cat $PdCl_2(dppe)$ or cat $PdCl_2(dppp)$	JOC 53 2984 (1988) (intramolecular)
	$N_2C(COR)CO_2R$, cat Cu	TL 29 5169 (1988) Bull Korean Chem Soc 12 461 (1991) (intramolecular)
	$N_2C(COR)CO_2R$, cat Cu(II)	Tetr 37 2079 (1981) JACS 106 6006 (1984); 109 4717, 6187 (1987) (all intramolecular) JOC 53 2984 (1988) (intramolecular)
	$N_2C(COR)CO_2R$, cat Cu(II) (enantioselective)	TL 31 6969 (1990) (intramolecular)

	$N_2C(COR)CO_2R$, cat semicorrin Cu (enantioselective)	SL 491 (1995) (intramolecular)
$C(CO_2R)_2$	$N_2C(CO_2R)_2$, cat $CuI \cdot P(OEt)_3$ $N_2C(CO_2R)_2$, cat $CuOTf$ $N_2C(CO_2R)_2$, cat bis(oxazoline)- $CuOTf$ (enantioselective) $BrCH(CO_2Et)_2$, DBU, $CuBr_2$ $Br_2C(CO_2R)_2$, Cu $Br_2C(CO_2R)_2$, $n-Bu_3Sb$ (on Michael acceptor) $MeSCl/NaCH(CO_2R)_2/Me_2SO_4/NaOEt$	JOC 58 879 (1993) (intramolecular) TL 36 4673 (1995) JOC 58 4479 (1993) (intramolecular) BCSJ 55 2687 (1982) Tetr 36 3517 (1980) TL 29 1033 (1988) Syn 690 (1980) JACS 106 5335 (1984)
$C(CO_2R)CN$	$Br_2C(CO_2R)CN$, $n-Bu_3Sb$ (on Michael acceptor)	TL 29 1033 (1988)
$CPhCO_2R(CN)$	$PhCHClCO_2R(CN)$, NaOH (on enones)	Syn 34 (1980)
CXY ($X, Y = CO_2Et, CN$)	Br_2CXY , Cu_2Br_2 , DMSO CH_2XY , I_2 , K_2CO_3 , phase transfer	BCSJ 54 2539 (1981) TL 31 7501 (1990)
$CHCN$	$(Me_3N^+CH_2CN)I^-$, NaH (on enones)	Syn 301 (1982)
$C(OCH_2Ph)CN$	$\begin{array}{c} N \\ \\ N-C-OCH_2Ph \\ \\ CN \end{array}$	TL 32 1925 (1991)
$CRNO_2$	N_2CRNO_2 , cat $Rh_2(OAc)_4$	TL 30 4197 (1989)
$CHPO(OEt)_2$	$N_2CHPO(OEt)_2$, cat $CuOTf$	TL 29 5033 (1988)
$C=C=CMe_2$	$Me_2CCIC\equiv CH$, KOH, dibenzo-18-crown-6	JOC 55 5232 (1990) TL 32 5547 (1991)
$C=C=C=CR_2$	$HC\equiv CC(OTf)=CR_2$, KO- <i>t</i> -Bu	Acct Chem Res 15 348 (1982)



JOC 55 4986 (1990)



TL 36 1121 (1995)



X = CHO, COR, CO₂R, CN; Y = COR, CO₂R; Z = H, R, CO₂R, Cl

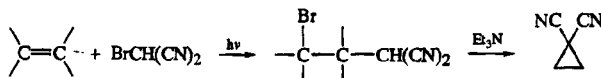
Ber 51 907, 533 (1918)

JACS 70 3470 (1948); 80 6568 (1958); 82 6416 (1960); 84 2246 (1962)

BSCF 986 (1957); 1102 (1959); 418, 788 (1960); 200 (1961); 2462 (1964)

JOC 24 1536 (1959); 25 2078 (1960); 27 4312 (1962); 29 240 (1964)

Compt Rend 248 887, 1465, 2840 (1959)

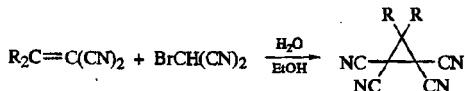


JACS 87 1394 (1965)

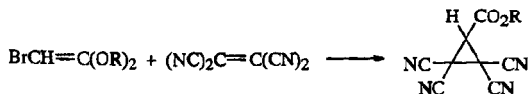
TL 1415 (1966); 4351 (1967)

JOC 31 2784 (1966)

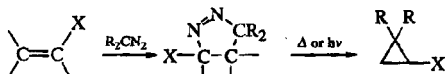
Ber 100 1281 (1967)



JOC 31 2784 (1966)



JOC 44 2038 (1979); 55 4963 (1990)



X = Ar, COR, CO₂R, CN

Reviews:

Newer Methods Prep Org Chem I 513 (1948)

Heterocyclic Compounds, Ed. R. Elderfield, J. Wiley, New York (1957), Vol 5

Houben-Weyl, Vol IV/3, p 43

Ber 21 2637 (1888); 23 701 (1890); 27 868, 877, 879 (1894); 36 3774, 3782 (1903); 49 1928 (1916);

70 1688 (1937); 71 2673 (1938); 88 49 (1955); 93 883, 1710 (1960); 100 3495 (1967)

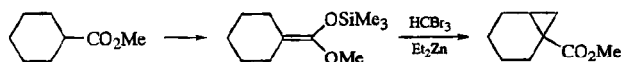
Ann 273 239 (1893); 496 252 (1932); 618 105 (1958); 678 78 (1964); 703 104 (1967)

J Prakt Chem [2] 133 291 (1932) (1,3-diene); [4] 36 73 (1967)

JACS 56 2710 (1934); 65 159 (1943); 72 3815 (1950); 73 2383 (1951); 79 4994 (1957); 80 6687

(1958); 81 3776, 5153, 5472 (1959); 82 3136, 5251 (1960); 84 869, 3736 (1962); 86 658 (1964); 87

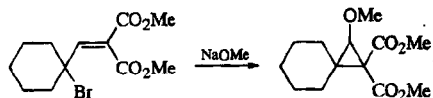
4119 (1965); 112 284 (1990)



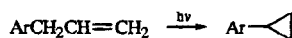
JACS 106 7283 (1984)



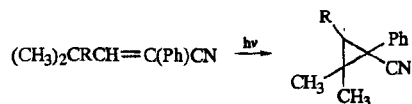
JCS Perkin I 751 (1981)



TL 34 7681 (1993)



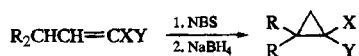
Chimia 35 52 (1981)



JOC 43 2839 (1978)

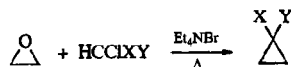
Can J Chem 60 1657 (1982)

TL 27 6225 (1986)

X, Y = CO₂R, CO₂R; CO₂R, CN; CN, CN

Syn 530 (1978)

JOC 59 8251 (1994)

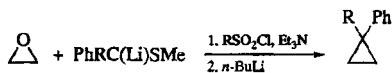


X, Y = F, F; F, Cl; Cl, Cl

Ber 100 1858 (1967)

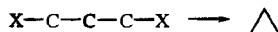
R = SR, SiMe₃

TL 30 7033 (1989)

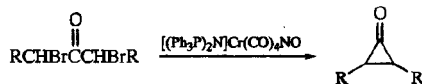


R = H, Me

SL 317 (1992)



See page 175, Section 5.



JACS 117 5592 (1995)



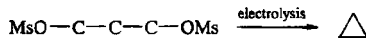
Mg

JACS 74 6290 (1952)

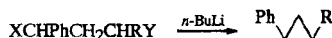
JOC 20 275 (1955)

EtMgBr, CoBr₂

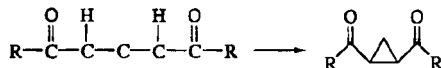
JACS 83 2734 (1961)



JOC 47 3090 (1982)

X = MeSe, *n*-Bu₃Sn; Y = Br, O₃SPh

TL 33 3381, 6527, 6529 (1992)

Br₂/KO-*t*-Bu

SL 276 (1991)

I₂, NaOH

Org Syn Coll Vol 6 401 (1988)

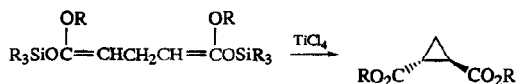
LDA/FeCl₃

TL 29 269 (1988)

Org Syn Coll Vol 8 467 (1993)

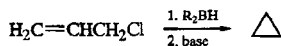
LDA/CuCl₂

SL 276 (1991)

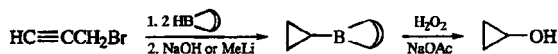


TL 23 799 (1982)

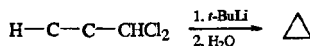
Tetr 39 847 (1983)



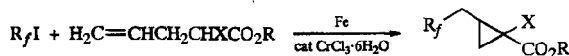
JACS 80 5830 (1958); 82 1886 (1960); 86 1791 (1964); 91 2149, 4306 (1969)
Israel J Chem 6 691 (1968)



JACS 91 4306 (1969)

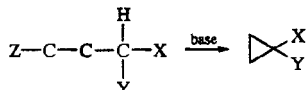


JACS 110 1305 (1988)



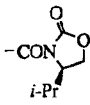
X = COR, CO₂R, CN

TL 34 5957 (1993)

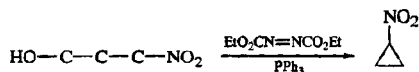


Review: Houben-Weyl, Vol IV/3, p 89

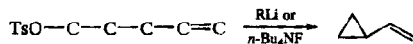
<u>X</u>	<u>Y</u>	<u>Z</u>	
COR	H, R	OTs	BSCF 1340, 1347 (1957) JACS 83 4678 (1961); 85 41 (1963) JCS C 909 (1967) JOC 37 2911 (1972)
		OTs, ⁺ NMe ₃	JOC 22 1146 (1957)
		OAc	JACS 80 1264, 5304 (1958)
		Cl	JOC 19 1628 (1954); 58 5802 (1993) JACS 78 112 (1956); 79 1455 (1957) BSCF 1634 (1962) Org Syn Coll Vol 4 597 (1963)
		Br	JCS Perkin II 579 (1982) JCS 1060 (1954); 2620 (1956) JACS 76 4115 (1954) Ber 91 768 (1958) JCS Perkin II 579 (1982)
CO ₂ R	H, R	I	JACS 87 4601 (1965)
		O ₃ SC ₆ H ₄ Br O ₂ CR	JOC 22 1146 (1957) TL 2441 (1976)

		Cl	Compt Rend 245 2304 (1957) BSCF 1487 (1964) Syn 955 (1982) (phase transfer) JOC 55 4333 (1990); 57 5959 (1992)
		Br	BSCF 681 (1957) SL 735 (1992)
CO ₂ R	CO ₂ R	Cl, Br, OTs	See page 175, Section 5.
	H, R	Cl	JOC 52 3168 (1987)
CN	H, R	OTs OTs, OMs O ₂ CR Cl	TL 32 939 (1991) BSCF 1854 (1961) BSCF 1476 (1964) JACS 67 1587 (1945); 109 7483 (1987) (bicyclobutane) TL 30 5017 (1989) TL 34 6025 (1993)
		Br	
CN	N=CPh ₂ N=CHPh	Cl Cl	JOC 55 4276 (1990) SL 151 (1991)
SO ₂ CF ₃	H, R	I	JACS 117 3272 (1995)
SO ₂ Ph	H, R	OMs	TL 22 4339 (1981); 31 6609 (1990); 32 531 (1991) JOC 57 2471 (1992) SL 866 (1995)
		I	
SO ₂ Ph	SO ₂ Ph	Cl, I	CC 1374 (1983) JCS Perkin II 605 (1986)
NO ₂	H, R	OMs	TL 34 1917 (1993) JOC 60 2968 (1995)

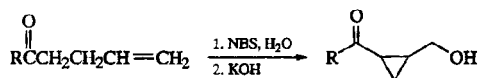
For analogous opening of epoxides, see page 1045, Section 4.1.



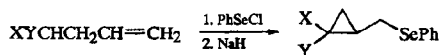
JOC 57 3757 (1992)



JOC 56 717 (1991)

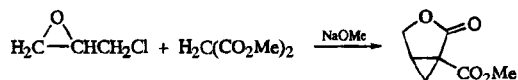


TL 34 7405 (1993)



X, Y = H, COR; H, CO₂R; CO₂R, CO₂R

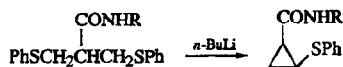
SL 965 (1994)



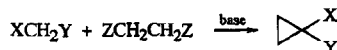
Helv 72 1301 (1989)



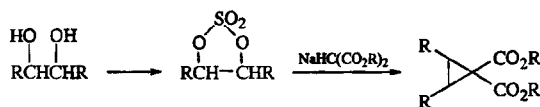
SL 599 (1993)



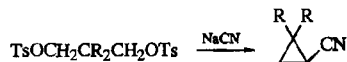
JACS 110 7185 (1988)



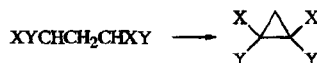
<u>X</u>	<u>Y</u>	<u>Z</u>	
H	NO ₂	Br	TL 34 1917 (1993)
CO ₂ R	CO ₂ R	OSO ₂ O	TL 36 2725 (1995)
CO ₂ R	CH=CHCO ₂ R	OSO ₂ O	TL 36 2725 (1995)
CO ₂ R, CN	Ar	Br	TL 27 3685 (1986)
CN	Ar	Cl	JACS 67 1249 (1945)
CN	N=CPh ₂	Br	JOC 57 6071 (1992)
CH=CHCH=CH		Br	JCS 646 (1958)



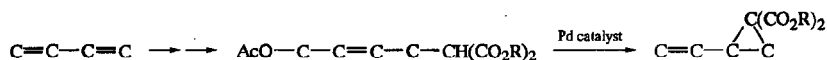
JACS 110 7538 (1988)



JACS 79 3467 (1957)



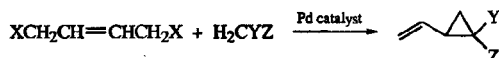
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
NO ₂	H	NaCH ₂ SOCH ₃ /I ₂	JACS 113 8807 (1991)
CN	CN	Br ₂	JOC 22 1130 (1957)
COR	H	Br ₂ /NaI	JCS 2620 (1956)



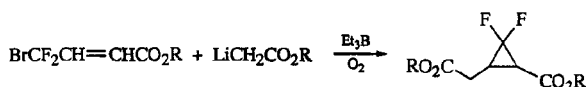
TL 21 3183 (1980); 23 5027 (1982); 26 2779 (1985)

JOC 46 2414 (1981); 52 5430 (1987)

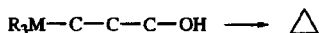
JACS 109 2176 (1987)



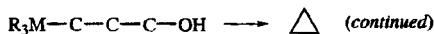
<u>X</u>	<u>Y</u>	<u>Z</u>	
Cl	CN	N=CPh ₂	TL 36 2979 (1995)
Br	SO ₂ Ph	SO ₂ Ph	TL 26 3049 (1985)
OCO ₂ Me	CO ₂ Me	CO ₂ Me	TL 26 3049, 3825 (1985); 29 669 (1988) (chiral) JACS 109 2176 (1987)



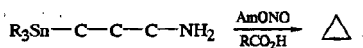
TL 35 913 (1994)



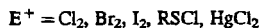
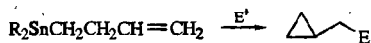
<u>M</u>	<u>Reagent(s)</u>	
Si	BF ₃ ·HOAc	JCS Perkin I 115 (1989) SL 121 (1995)
Sn	Lewis acid	TL 36 471 (1995)
	BF ₃ ·OEt ₂	CL 1897 (1984)
	BF ₃ ·HOAc	TL 24 4591 (1983) JOMC 285 173 (1985)
	PCl ₃	JOMC 25 C13 (1970)
	Ph ₃ P	CL 1897 (1984)
	Ph ₃ PBr ₂	CL 1123 (1974)
	SOCl ₂	JOMC 25 C13 (1970)
	SOCl ₂ , Et ₃ N	SL 121 (1995)
	SOCl ₂ , py	TL 23 2577 (1982); 25 5255 (1984)
	TsCl/Δ or HOAc	JOC 52 1493 (1987)
	MsCl, Et ₃ N	JACS 92 6990 (1970) SL 653 (1995)

**M**Reagent(s)

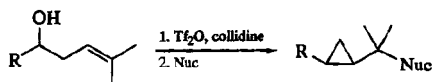
MsCl, py	CL 1897 (1994)
Tf ₂ O, Et ₃ N or py	SL 653 (1995)
MeO ₂ CN ⁺ SO ₂ NEt ₃	SL 653 (1995)



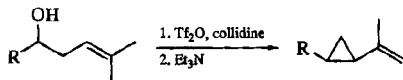
CL 1333 (1975)



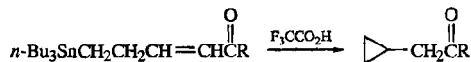
JOMC 73 237 (1974)

Nuc = *i*-Bu₃Al (Nuc = H), Me₃Al, Et₂AlCN, H₂O, ROH, RSH, *i*-Bu₂AlSePh, Me₃SiN₃

SL 739 (1995)



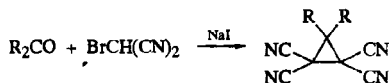
SL 739, 1023 (1995)



TL 23 2577 (1982)



TL 32 2655 (1991); 34 5795 (1993)

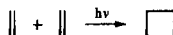


Arkiv Kemi 14B 37 (1941)

JOC 28 1220 (1963)

2. Four-Membered Rings

Review: Houben-Weyl, Vol IV/4 (1971)



Reviews:

- Chem Rev 66 373 (1966) (intramolecular); 88 1453 (1988) (intramolecular, enones); 93 3 (1993) (enones)
 Acct Chem Res 1 50 (1968) (enones); 4 41 (1971) (enone photoannulation); 15 135 (1982) (intramolecular)
 Chem Rev 69 845 (1969) (dienes and polyenes)
 Syn 287 (1970) (enones)
 Photochem Photobiol 25 605 (1977)
 Org Photochem 5 123 (1981); 10 1 (1989) (intramolecular)
 Rev Chem Intermed 4 369 (1981)
 A. C. Weedon in "Synthetic Organic Photochemistry," Ed. W. M. Horspool, Plenum, New York (1984), Chpt 2
 Topics Curr Chem 133 83 (1986)
 "Organic Photochemistry," Ed. A. Padwa, Marcel Dekker, New York (1989), Chpt 1 (enones, intramolecular)
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 2.3, p 123
 Org Rxs 44 297 (1993) (enones)
 SL 884 (1994) (intramolecular, cyclophanes)
 Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21c, G. Thieme, Stuttgart-New York (1995), p 3085

Recent references:

Intramolecular

- JACS 101 3961 (1979) (CuOTf catalyzed); 103 82 (1981); 104 998, 6841 (1982); 105 1292, 1299 (1983); 107 5732 (1985); 108 800, 1311 [Cu(I) catalyzed], 3385, 3435, 6425 (1986); 109 2212, 2523, 2850, 6199, 7230 (1987); 110 5547 (1988); 111 4852, 5824 (1989); 112 8971 (1990); 113 657 (1991) [Cu(I) catalyzed]; 113 3085, 3485, 3490, 8839 (1991); 114 5445, 8725, 9673 (1992); 115 3146 (1993)
 CC 235 (1979); 1195 (1980); 118 (1981); 1578 (1987)
 Helv 63 1198 (1980)
 Org Photochem 5 123 (1981) (enones, review)
 JOC 46 4821 (1981); 47 331, 829, 3121, 3297 (allene), 3597 (2-alken-4-olide), 3893 (1982); 50 3155 (1985) (allene); 52 83 [Cu(I) catalyzed], 2346, 2644, 3603 (1987); 53 2647, 3673 (1988); 54 1635, 3158 (1989); 56 4537, 7150 (1991); 57 4632, 5708, 5955 (1992); 58 1501, 6208 (1993); 59 1333, 6476, 6490 (1994); 60 1381, 2526, 6883, 7256 (Cu catalyzed) (1995)
 Tetr 37 4543 (1981)
 Can J Chem 60 425 (1982)
 Acct Chem Res 15 135 (1982) (review)
 J Chem Ed 59 313 (1982) (review)
 TL 23 23 (enones), 711 (1982); 24 2961 (1983); 26 989 (allene), 1429 (allene), 5883 (1985); 27 2703 (allene), 5177, 6393 (1986); 28 1295, 5083, 5087, 5497 (1987); 29 4691, 5375 (1988); 30 2661, 4429, 5211, 5439, 5997 (1989); 31 97, 107 (1990); 32 2105, 2367, 6969 (1991); 33 1013, 2795, 5563, 7347 (1992); 34 199, 635, 4565, 5555, 6127 (1993); 35 261, 1657, 3953 (1994); 36 1921, 6523 (1995)

JCS Perkin I 1905 (1983)

Org Syn Coll Vol 7 177 (1990) (CuOTf catalyzed)

SL 145, 776 (1995)

Intermolecular

JACS 102 3634 (1980); 107 1308 (1985); 108 306 (1986); 110 8111 (1,3-dienes, enamides), 8261 (enones) (1988); 111 3707 (1989) (enone); 112 239 (enone), 775 (allene, enone), 5672, 8889 (1990); 113 3085, 3533, 3904, 4607, 8525 (enone regioselectivity) (1991); 114 2567, 9673 (1992); 115 7009 (1993) (enone regioselectivity); 116 10870 (1994); 117 5647, 9804 (1995)

Can J Chem 60 425 (micelles), 872 (allene + 2-alken-5-olide) (1982)

JCS Perkin I 1697 (1984)

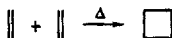
JOC 50 3026 (1985); 51 5226 (1986); 52 1993, 2639, 3595 (1987); 53 1519, 2624 (1988); 54 587, 601, 1805 (1989); 55 1506, 4933 (1990); 56 463, 561 (1991); 57 599, 1467, 3292, 4255, 5370 (1992); 58 1491, 6548, 7388 (1993); 59 6476 (1994); 60 1924, 2183 (1995)

TL 26 4707, 6163 (1985); 27 5975, 6049 (1986); 28 581 (allene), 2833 (chiral), 2857, 5017 (1987); 29 2613, 6881 (1988); 31 47, 1573 (1990); 32 4177 (1991); 33 6465 (1992); 34 5313, 7455, 7517 (1993); 35 3883 (1994); 36 6083, 6087 (1995)

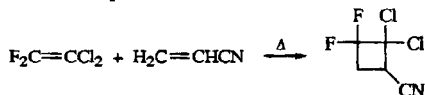
Tetr 42 3547 (1986)

Org Syn Coll Vol 6 1024 (1988); 7 315 (1990)

SL 957 (1995)

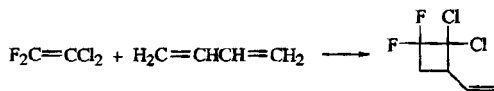


Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 2.1, p 63



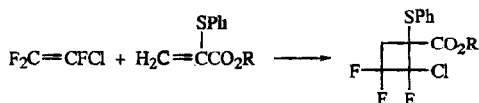
Org Rxs 12 1 (1962) (review)

JOC 52 1872 (1987)

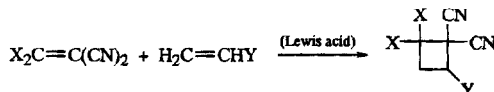


Org Rxs 12 1 (1962) (review)

JACS 71 490 (1949); 86 616 (1964)



TL 32 7265 (1991)



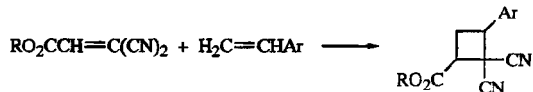
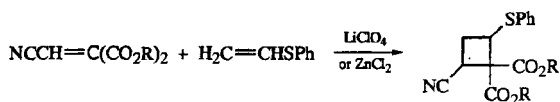
X = CF₃, CN, CO₂R; Y = OR, SR, Ar

Acct Chem Res 10 117, 199 (1997)

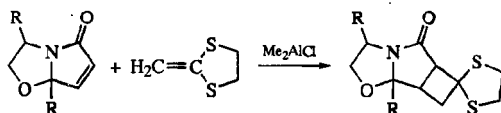
Rec Trav Chim 105 71 (1986)

TL 31 2553, 2557, 2561 (1990)

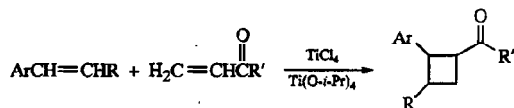
JOC 59 5424 (1994)



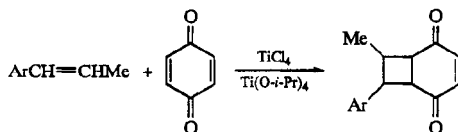
JOC 58 4185 (1993); 59 5424 (1994)



JOC 60 4359 (1995)



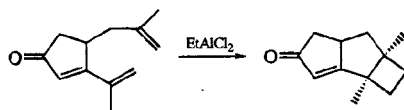
TL 30 1761 (1989)



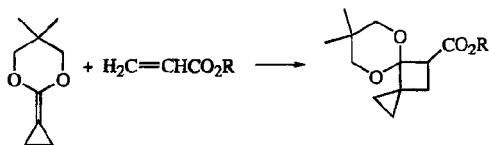
JACS 110 7931 (1988); 113 5068 (1991) (chiral)

TL 34 1429 (1993)

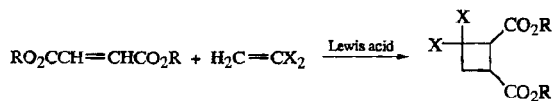
JOC 59 6567, 6588 (1994)



TL 31 2242 (1990)



JACS 116 1123 (1994)

X

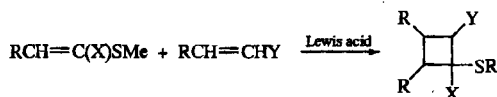
OR

TL 30 6453 (1989); 32 6997 (1991)

SL 197 (1993)

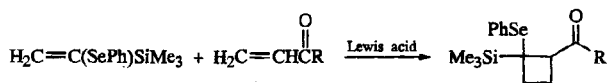
SR

SL 197 (1993)

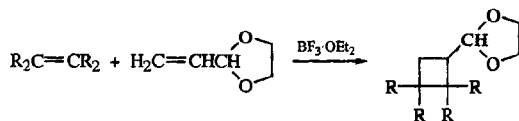
X = alkyl, SMe; Y = CO₂R, CN, imide

CL 793 (1989); 1295 (1990)

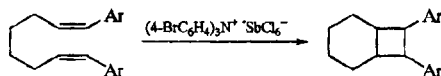
JACS 114 8869 (1992)



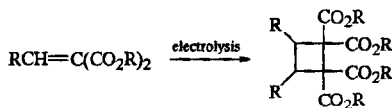
JOC 57 5610 (1992)



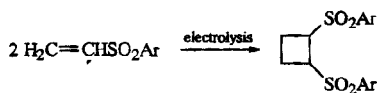
TL 33 157 (1992)



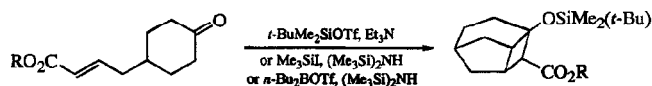
JACS 114 10968 (1992)



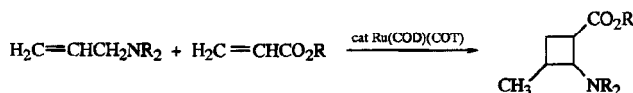
TL 33 3223 (1992)



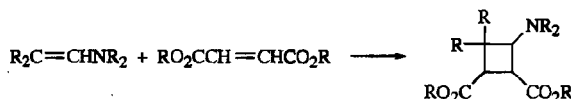
TL 31 667 (1990)



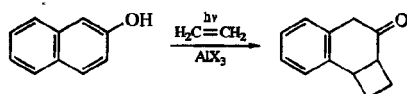
JACS 114 4408 (1992); 115 8107 (1993)
 TL 35 1901 (1994); 36 8071 (1995)



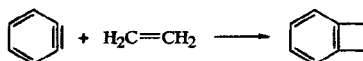
TL 33 5533 (1992)



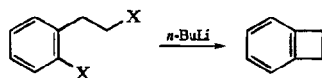
JOC 57 594 (1992)



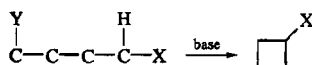
TL 30 6193 (1989)
 JOC 58 2797 (1993)



Chem Rev 70 471 (1970) (review)
 JOC 38 522 (1973); 40 1355 (1975); 47 2393, 2396 (1982); 54 1435 (1989)
 TL 4111 (1976)
 Austral J Chem 31 2003 (1978)



JOC 41 1184 (1976)
 TL 4573 (1977)
 JACS 109 7137 (1987)
 Org Syn Coll Vol 7 326 (1990)

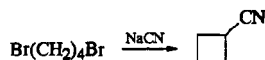


<u>X</u>	<u>Y</u>	
COR	Cl	IACS 83 938 (1961) TL 2525 (1964) Ber 100 720 (1967) JCS C 2350 (1969)
		Br
		Br
		I
	O ₃ SC ₆ H ₅ OTs	Angew Int 1 457 (1962) Tetr 26 1589 (1970) JOC 27 1883 (1962) Angew Int 1 457 (1962) TL 1043 (1963); 2525 (1964); 2043 (1966); 3627 (1969) IACS 88 4110 (1966); 89 4133 (1967) BSCF 147 (1966) Ber 100 720, 2978 (1967) Tetr 25 5267 (1969); 26 1589 (1970) JOC 37 2911 (1972) Angew Int 1 457 (1962) Ber 100 720 (1967)
		⁺ NMe ₃
		OMs
		OTs
		JOC 34 3837 (1969) Tetr 25 5281 (1969)
		Cl
enone		BSCF 1833 (1959); 979 (1960) JOC 59 6098 (1994)
CO ₂ R	Cl	CA 37 4705 ⁶ (1943) Zh Obshch Khim 22 122 (1952) [CA 46 11119d (1952)] Bull Acad Sci USSR, Div Chem Sci 1585 (1966)
(CO ₂ R) ₂	Cl	IACS 71 2941 (1949); 106 1051 (1984) JOC 26 2335 (1961)
	Br	
CN	Cl	Compt Rend 231 703 (1950) BSCF 1833 (1959) BSCF 979 (1960)
	OTs	
	Cl	JOC 33 300 (1968)
1,3-dithiane	Cl, I	CC 1374 (1983) JCS Perkin II 605 (1986)
(SO ₂ Ph) ₂		
⁺ PPh ₃	Br	JOC 30 3215 (1965); 33 3082 (1968)

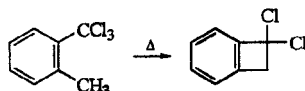


X = halogen, OTs

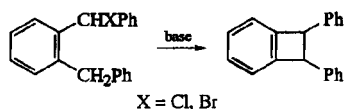
JCS 51 1 (1887); 61 36 (1892); 127 2387 (1925); 1487 (1929); 1211 (1938); 3002 (1953)
 Ber 40 3883 (1907); 98 2651 (1965); 99 1509 (1966)
 Rec Trav Chim 50 921 (1931)
 JACS 63 1698 (1941); 84 4982 (1962)
 JOC 14 1036 (1949); 21 1371 (1956); 22 1029 (1957); 26 54 (1961); 27 1647 (1962); 30 1945, 3308, 4212 (1965); 31 4069 (1966)
 Org Syn Coll Vol 3 213 (1955); 4 288 (1963)
 Ann 648 36 (1961); 666 81 (1963); 678 53 (1964); 685 74 (1965); 692 53 (1966); 694 1 (1966)
 Naturwiss 50 441 (1963)
 Angew Int 5 127 (1966)
 Bull Acad Sci USSR, Div Chem Sci 1585 (1966)



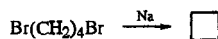
Tetr Suppl 8 I 279 (1966)



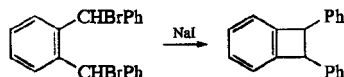
JACS 82 749 (1960)
 JOC 31 2244 (1966); 34 2906 (1969)



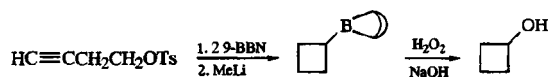
JACS 80 6149 (1958); 85 4031 (1963)



Tetr Suppl 8 I 279 (1966)

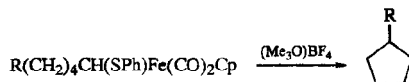


JACS 80 6149 (1958)



JACS 91 4306 (1969)

3. Five-Membered Rings



JACS 111 8527 (1989)

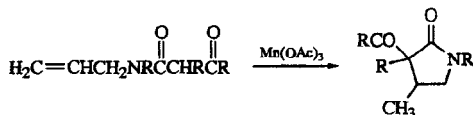
JOC 55 5820 (1990)

TL 32 5753 (1991)

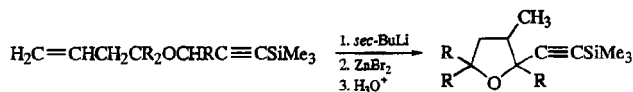


TL 33 1675 (1992)

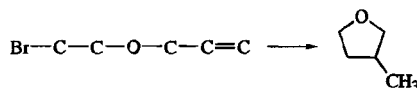
JOC 58 1415 (1993); 60 8101 (1995)



TL 30 4531 (1989)



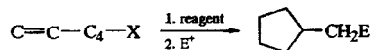
TL 36 1263 (1995)

 $\text{h}\nu$, Et_3N

TL 35 8161 (1994)

 $\text{Cr}(\text{OAc})_2$, H_2O

SL 44 (1990)

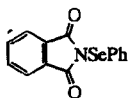
For R_3SnH , see page 175, Section 5.

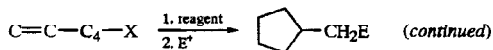
X


Reagent(s)

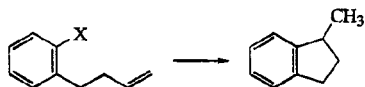
 E^+

1

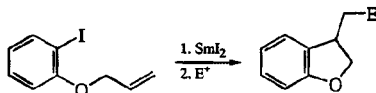
 $t\text{-BuLi}$ MeOH , MeOD , CO_2 , O_2 JACS 109 2442 (1987);
113 5720 (1991)JOC 53 1337 (1988); 59
6528 (1994)
TL 33 903, 6243 (1992)



<u>X</u>	<u>Reagent(s)</u>	<u>E⁺</u>	
	Zn	H ₂ O, I ₂ , CuCN·2LiCl / HC≡CCO ₂ R or RCOCl	TL 34 6053 (1993) SL 266 (1993)
	Et ₂ Zn	H ₂ O, I ₂ , CuCN·2LiCl / HC≡CCO ₂ R	SL 266 (1993)
	Et ₂ Zn, cat Ni(acac) ₂	CuCN·2LiCl / E ⁺ [E ⁺ = H ₂ C=C(CH ₂ Br)CO ₂ Et, HC≡CCO ₂ Et, PhCH=C(CO ₂ Et) ₂ , 	TL 35 8349 (1994)
	Et ₂ Zn, cat PdCl ₂ (dppf)	O ₂ CuCN·2LiCl / E ⁺ [E ⁺ = RX (R = allylic, vinylic), HC≡CCO ₂ R, enone, RCOCl, RCH=CHNO ₂]	TL 36 231 (1995) JACS 115 7027 (1993) TL 34 7911 (1993)
SeMe	RLi	H ₂ O, RCHO, CO ₂	CC 1214 (1987) SL 511 (1990); 907 (1992) Tetr 50 7177 (1994) TL 36 7917, 8111 (1995)

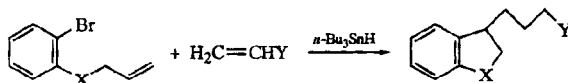


<u>X</u>	<u>Reagent(s)</u>	
F, Cl, Br, I	Li, Na or K; <i>t</i> -BuOH	JACS 108 4899 (1986)
	<i>n</i> -BuLi / H ₂ O	JACS 111 2434 (1989)
	cat Pd(OAc) ₂ , cat PPh ₃ , HCO ₂ ⁻	TL 29 4329 (1988)
	NaBH ₄ , cat 10-methyl-9,10-dihydroacridine, hv	TL 33 6587 (1992)
	<i>n</i> -Bu ₃ SnH	See page 175, Section 5.
	electrolysis	JACS 108 1441 (1986) JOC 54 5953 (1989)
	electrolysis, cat Ni(II)	TL 35 725 (1994)
OMe	electrolysis	JACS 111 2434 (1989)



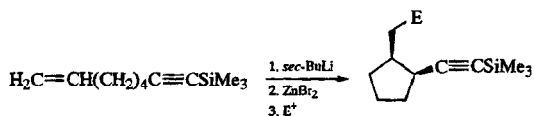
E⁺ = H₂O, D₂O, I₂, (PhS)₂, (PhSe)₂, R₃SnI, RCHO, R₂CO

SL 773 (1990)



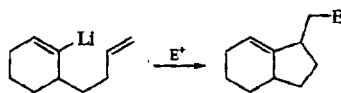
X = O, NCOR; Y = Ph, CO₂R, CN, SO₂Ph

TL 29 4133 (1988)



E⁺ = H₂O, I₂, H₂C=CHCH₂Br [CuCN], RCH=CHI [cat Pd(PPh₃)₄]

JOC 60 863 (1995)

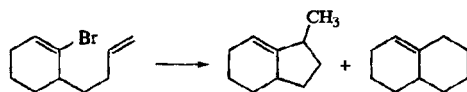


E⁺ = H₂O, RBr, H₂C=CH₂, DMF, CO₂

JACS 110 4788 (1988)



TL 31 6911 (1990)

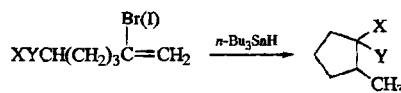


electrolysis, cat Ni(II)

TL 35 725 (1994)

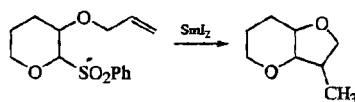
n-Bu₃SnH

JACS 110 4788 (1988)

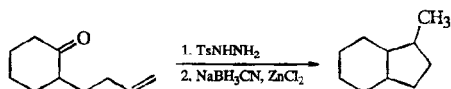


X, Y = H, OR; OR, OR; CO₂R, CO₂R; H, CO₂R; H, Ph

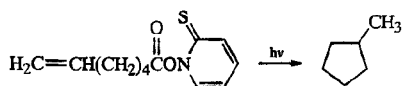
JACS 110 5900 (1988); 115 6051 (1993)



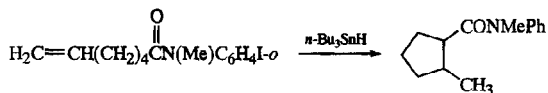
TL 33 8065 (1992)



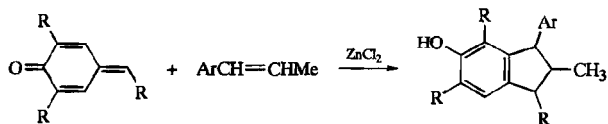
TL 34 6209 (1993)



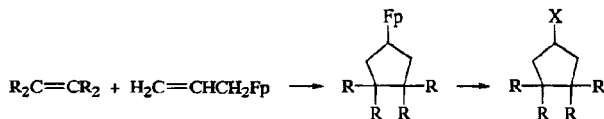
TL 30 2983 (1989)



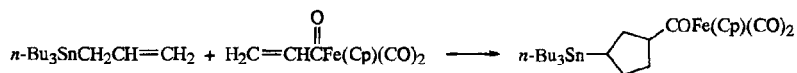
JOC 56 4335 (1991)



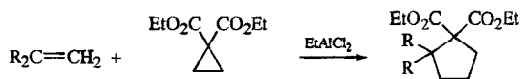
JOC 55 3708 (1990)

R = H, CN, CO₂R; Fp = CpFe(CO)₂; X = H, Br, CO₂R'

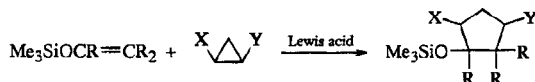
JCS Perkin I 285, 295, 301 (1982)



SL 1 (1991) (review)

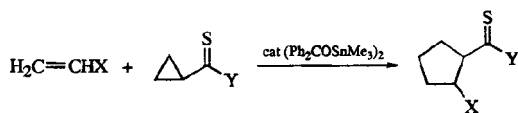


JOC 51 4391 (1986)

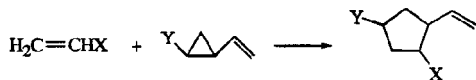
X
COCH₃Y
OMe
SPh
OBu

Lewis acid

SnCl₄
Me₂AlCl
SnCl₄SL 771 (1991)
TL 34 6077 (1993)
SL 771 (1991)



JOC 59 1129 (1994)

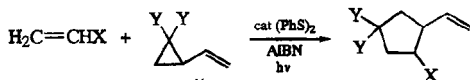
 $\text{X} = \text{R, OR, O}_2\text{CR, CO}_2\text{R, CN; Y} = \text{COR, CO}_2\text{R, CN, SO}_2\text{Ph}$

cat PhSH

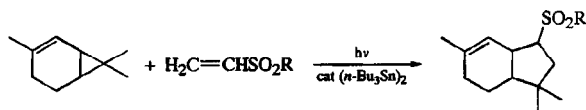
TL 29 5135 (1988)

cat (PhS)₂, cat AIBN, cat Me₃Al

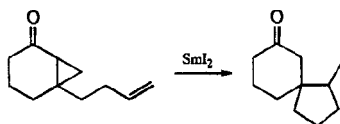
JACS 110 3300 (1988)

 $\text{X} = \text{CO}_2\text{R, CN; Y} = \text{Cl, Br}$

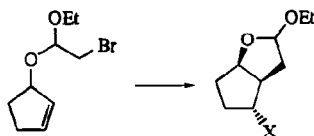
JACS 115 11364 (1993)



SL 273 (1994)



TL 32 6211, 6649 (1991)

XReagent(s)

H

n-Bu₃SnH
cat vitamin B₁₂, electrolysisSee page 175, Section 5.
TL 28 1313, 1317 (1987)

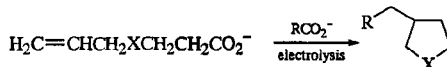
CN

(Ph₃Sn)₂, *t*-BuCNJACS 105 6765 (1983), 111 3450
(1989)*n*-Bu₃SnCl, NaBH₃CN,
t-BuCN

JACS 108 303 (1986)

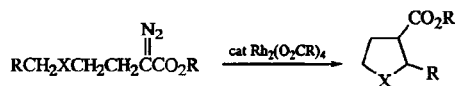
$\text{CH}_2\text{CH}_2\text{CN}$	$n\text{-Bu}_3\text{SnH}$, $\text{H}_2\text{C}=\text{CHCN}$	JACS 111 3450 (1989)
CHRCH_2COR	$n\text{-Bu}_3\text{SnH}$, enone	JACS 111 3450 (1989)
$\text{CH}_2\text{CH}_2\text{X}$ ($\text{X} = \text{CN}$, CO_2Me , COEt , $\text{PO}(\text{OEt})_2$, SO_2R)	$n\text{-Bu}_3\text{SnCl}$, NaBH_3CN , $\text{H}_2\text{C}=\text{CHX}$	JACS 108 303 (1986)
$\text{CH}_2\text{CH}=\text{CH}_2$	$n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2$	JACS 111 3450 (1989)

See also page 175, Section 5.



Angew Int 23 981 (1984) ($\text{X} = \text{O}$)

TL 29 2797 ($\text{X} = \text{NR}$), 2801 ($\text{X} = \text{O}$) (1988)



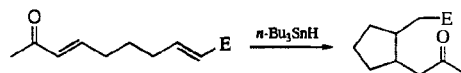
X

O

TL 36 2587 (1995)

CH_2

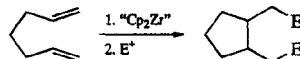
JACS 117 5757 (1995)



$\text{E} = \text{COR}$, CO_2R , CN

JACS 113 7784 (1991)

JOC 60 4850 (1995)



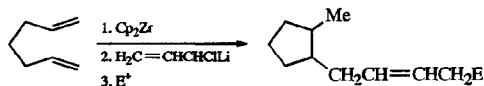
$\text{E}^+ = \text{H}_2\text{O}$, Br_2 , I_2 , O_2 , S_2Cl_2 , Se_2Cl_2 , Ph_2SnCl_2

JACS 111 6435 (1989); 113 6268 (1991); 116 1845, 1880, 9457 (1994)

TL 30 5105 (1989); 33 7735 (1992); 34 3359 (1993)

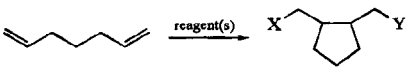
JOC 59 4542 (1994)

SL 451 (1994), 1237 (1995)

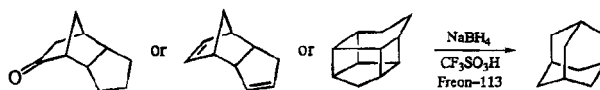


$\text{E}^+ = \text{H}^+$, RCHO

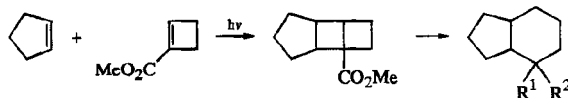
TL 35 785 (1994)

			
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
H	H	<i>i</i> -PrMgCl, Ti(O- <i>i</i> -Pr) ₄ /HCl	TL 36 4261 (1995)
	R _f	R _f /I, Zn, cat YbCl ₃	TL 34 1321 (1993)
	SiX ₃ (X = Et, Cl)	HSiX ₃ , (<i>t</i> -BuO) ₂	TL 31 5265 (1990)
	Si(SiMe ₃) ₃	HSi(SiMe ₃) ₃ , hν	SL 91 (1990)
	SnMe ₃	Me ₃ SnCl, NaBH ₃ CN	SL 402 (1992)
	SCoCH ₃	CH ₃ COSH, AIBN	JACS 114 3115 (1992)
	PPh ₂	Ph ₂ PH, AIBN	JOC 50 5620 (1985)
			TL 34 1215 (1993)
Cl	Ts	TsCl, (PhCO ₂) ₂	TL 30 6369 (1989)
			JOC 60 6040 (1995)
Cl, Br	SO ₂ R	RSO ₂ X, hν or CuCl	Tetr 23 7119 (1988)
Br	Ts	TsBr, hν	Tetr 46 5285 (1990); 47 9463 (1991)
			JOC 57 6118 (1992); 60 6040 (1995)
I	CH ₂ CO ₂ Et	ICH ₂ CO ₂ Et, cat Cr(OAc) ₂	SL 861 (1991)
	CF ₂ CF=CF ₂	ICF ₂ CF=CF ₂ , Cu	SL 141 (1992)
	Ts	TsI, hν	Tetr 47 9463 (1991)
Ts	CH ₂ C(=CH ₂)COR	TsCH ₂ C(=CH ₂)COR	SL 527 (1990)
PhSe	Ts	PhSeTs, AIBN, (<i>n</i> -Bu ₃ SnH)	TL 34 1219 (1993)
	CH(CO ₂ R) ₂	PhSeCH(CO ₂ R) ₂ , hν	JOC 60 6040 (1995)
			JOC 58 3355 (1991)

4. Six-Membered Rings

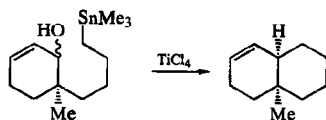


JOC 54 1450 (1989)



R¹, R² = H, CH₂OH; H, CO₂Me; Me, CO₂Me

JACS 100 4321 (1978)



TL 22 2077 (1981)
JACS 103 6767 (1981)

XYBase SO_2Ar MsO

LDA

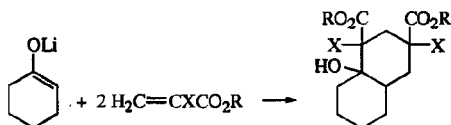
JOC 51 5311 (1986)

 TsO $n\text{-BuLi}$

JACS 111 3363 (1989)

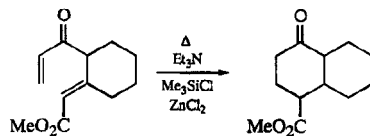
 NO_2 I NaOMe

TL 30 4141 (1989)



$\text{X} = \text{H}, \text{R}, \text{Br}, \text{ArS}, \text{SiMe}_3$

JACS 108 511 (1986)



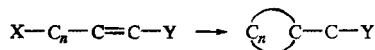
TL 25 2167 (1984)

CC 1159 (1985); 721, 1467 (1987)

JCS Perkin I 1543 (1986)

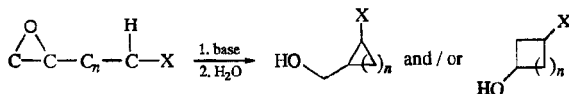
5. Various Ring Sizes

For a review of free radical cyclizations, see Org Rxs 48 301 (1996).

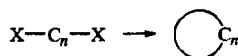


$\text{X} = \text{Br}, \text{I}; \text{Y} = \text{COR}, \text{CO}_2\text{R}, \text{CN}$

See the appropriate functional group Y for conjugate addition reactions.



See page 1045, Section 4.1.



Reviews:

 $n=3$ Houben-Weyl, Vol IV/4 (1971), p 32
Russ Chem Rev 51 368 (1982) $n=4$

Houben-Weyl, Vol IV/4 (1971), p 31

Reagent(s)n

electrolysis

3, 4

TL 1119 (1974)
Org Syn Coll Vol 6 153 (1988)

Li(Hg)

3-5

TL 4925 (1967); 28 5263 (1987)
JACS 110 1356 (1988)

MeLi

3

TL 28 5411 (1987)

n-BuLi

6

JOC 59 2043 (1994)

t-BuLi

3-5

TL 23 5123 (1982)

PhLi

8

TL 29 1521 (1988)

Na

3

TL 2173 (1963)
Org Syn Coll Vol 6 133 (1988)
JOC 59 4362 (1994)

4

Tetr Suppl 8 I 279 (1966)

Na, C₁₀H₈

8

TL 29 1521 (1988)

Na, Ph₂C=CPh₂

10

JOC 33 3277 (1968); 46 1543
(1981); 55 2404 (1990)

Mg

3

JACS 75 3344 (1953); 110 8500
(1988)

5

JOC 59 2043 (1994)

Mg/AgOTf

4-6

JOC 41 2882 (1976)

RMgBr, FeCl₃

3

JACS 83 3232 (1961)
JOC 29 2813 (1964)Cr(ClO₄)₂, EDA

3

JOC 33 1027 (1968)

Ni(COD)₂, bipy

3-6

CL 1363 (1974)

Zn

3

J Prakt Chem 36 300 (1887); 58
458 (1898)

Ind Eng Chem 28 1178 (1936)

JACS 66 812 (1944); 68 1335
(1946); 70 946 (1948)JOC 23 1715 (1958); 58 7709
(1993)

BSCF 116 (1966)

Syn Commun 11 865 (1981)

Zn-Cu

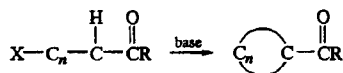
3

Org Syn 44 30 (1964)

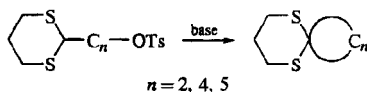
CuI·PR₃ (R = Et, *n*-Bu),

3 > 5 > 6 > 4

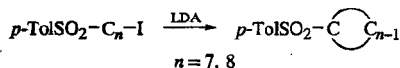
JOC 55 584 (1990)

LiC₁₀H₈

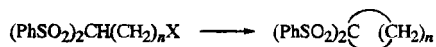
\underline{n}	\underline{X}	
4	Cl	JCS Perkin II 579 (1982)
	Br	Ber 91 1616 (1958)
5		JCS Perkin II 579 (1982)
	Br	Ber 91 1616 (1958)



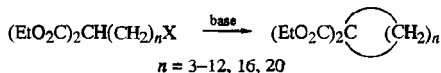
JOC 56 6038 (1991); 59 6063 (1994)



TL 35 3401 (1994)



\underline{X}	<u>Reagent(s)</u>	\underline{n}	
halogen	NaOEt	2-6	CC 1374 (1983)
			JCS Perkin II 605 (1986)
OH	EtO ₂ CN=NC ₂ Et, PPh ₃	2-6	JOC 58 5892 (1993)
$\overset{+}{S}(\text{Et})\text{Ar}$	NaOEt	2-4	Gazz Chim Ital 118 233 (1988)

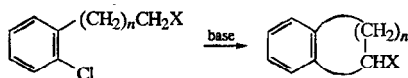


Arzneim Forsch 16 1571 (1966)

JCS B 67 (1968)

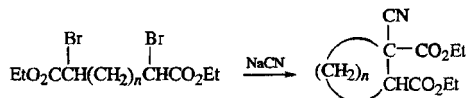
JACS 106 1051 (1984)

JOC 59 5336 (1994)



X (ring size) = PhCO (5), CO₂Et (4-6), CN (4-7), SO₂Ph (4, 5)

JOC 27 3836 (1962); 55 3622 (1990)



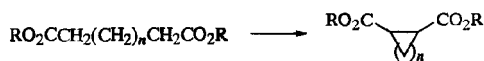
\underline{n}

2

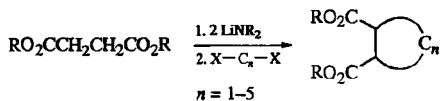
2-4

JACS 51 1536 (1929); 64 2696 (1942)

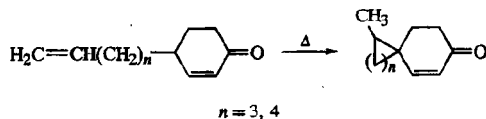
JOC 30 1206 (1965)



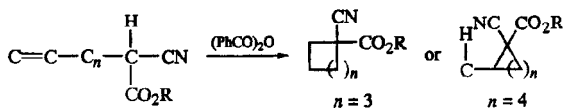
See page 1724, Section 2.



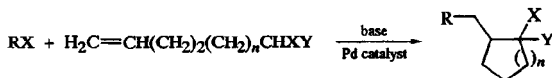
See page 1724, Section 2.



TL 30 4329 (1989)



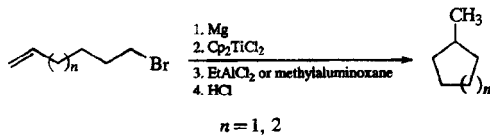
BSCF 3070 (1970)



R = aryl, vinylic; $n = 1, 2$; X, Y = COR, CO₂R; SO₂R, CO₂R; CO₂R, CO₂R; CN, CO₂R; SO₂R, CN; CN, CN

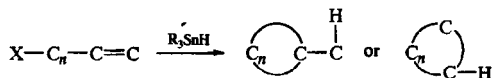
TL 30 69 (1989); 32 1641 (1991); 36 8019 (1995)

Tetr 46 7763 (1990); 48 3891 (1992); 50 403 (1994)



JACS 112 9441 (1990); 114 4936 (1992); 116 8912 (1994)

Organomet 9 3022 (1990)



Reviews and key references:

- Acct Chem Res 4 386 (1971); 24 139 (1991) (stereochemistry)
 Pure Appl Chem 40 553 (1974) (mechanism)
 A. L. J. Beckwith and K. U. Ingold in "Rearrangements in Ground and Excited States," Ed. P. de Mayo, Academic Press, New York (1980), pp 162-310
 CC 482 (1980) (steric and stereoelectronic effects)
 Tetr 37 3073 (1981); 41 3925 (1986) (theory)
 J.-M. Surzur in "Reactive Intermediates," Ed. R. A. Abramovitch, Plenum, New York (1981), Vol 2, Chpt 3
 Angew Int 22 753 (1983); 24 553 (1985)
 Science 223 883 (1984)
 Tetr Symposia-in-Print No. 22 41 3887-4302 (1985)
 B. Giese, "Radicals in Organic Synthesis - Formation of Carbon-Carbon Bonds," Pergamon Press, New York (1986)
 Curr Sci 56 392 (1987)
 D. P. Curran in "Advances in Free Radical Chemistry," Ed. D. D. Tanner, Vol 1, JAI, Greenwich, CT (1990)
 BSCF 695 (1990)
 Chem Rev 91 1237 (1991)
 Org Rxs 48 301 (1996)



XRing size

halogen

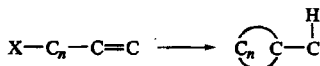
5

- JACS 96 1613 (1974); 104 5564 (1982)
 (2-alkoxytetrahydrofurans); 105 3741, 6765
 (subsequent radical trapping) (1983) (both bi-
 cyclic acetals); 107 500 (2-alkoxytetrahydro-
 furans), 1448 (serial cyclization) (1985); 108 303
 (2-alkoxytetrahydrofuran, subsequent radical
 trapping), 1106 (serial cyclization), 1708 (serial
 cyclization), 2116 (serial cyclization), 3102,
 5890 (dihydrobenzofurans), 8098 (1986); 111
 3450 (bicyclic acetal, subsequent radical trap-
 ping), 6849 (ultrasound), 7507 (1989); 112 5601
 (1990); 114 9318 (1992) (dihydroindole); 116
 8430 (1994)
 J Chem Res (S) 78 (1981)
 Austral J Chem 36 545 (1983) (rates,
 stereochemistry)
 CC 1445 (1983) (tetrahydroindanes); 115 (1986)
 (oxindoles); 1456 (1987) (bicyclic alkane)
 JOC 48 1782 (1983); 50 546, 5620 (pyrrolidines),
 5875 (1985); 51 4708 (1986) (tetrahydrofurans);
 54 1157, 1997, 3981 (tetrahydrofuran), 5350
 (serial cyclization) (1989); 55 791 (serial cycli-
 zation), 1786 (spirocyclization) (1990); 56 1320
 (1991) (2-alkoxytetrahydrofuran); 57 2873
 (1992) (dihydroindole); 58 2442 (1993) (dihy-
 droindole); 59 1396, 6999 (2-alkoxytetrahydro-
 furan) (1994); 60 2607 (dihydrobenzofuran),
 3859 (siloxane), 3871 (2-alkoxytetrahydrofuran,
 siloxane) (1995)

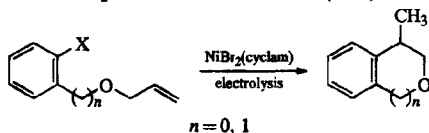
<u>X</u>	<u>Ring size</u>	
halogen (<i>continued</i>)	5 (<i>continued</i>)	<p>TL 25 4317 (1984) (2-alkoxytetrahydrofurans); 26 957 (pyrrolidines), 3349 (serial cyclization, <i>n</i>-Bu₃GeH), 4991 (serial cyclization) (1985); 27 3715 (1986) (tetrahydrofurans); 28 671 (2-alkoxytetrahydrofurans), 1317 (2-alkoxytetrahydrofurans), 1623 (2-alkoxytetrahydrofurans), 2127, 3953 (pyrrolidines), 6389 (oxindole) (1987); 29 45 (dihydroindoles), 321 (tetrahydrofuran), 391 (indane), 2413 (2-alkoxytetrahydrofuran), 4001 (siloxane), 4685 (dihydrobenzofuran), 6219, 6585 (tetrahydrofuran), 6657 (oxindole) (1988); 30 57 (tetrahydrofuran), 2657 (oxindole), 3369, 3609 (2-alkoxytetrahydrofuran, siloxane), 4363 (lactone) (1989); 31 2193, 3745 (bicyclic ketone), 6047 (1990); 32 1737 (2,3-dihydrobenzofurans and -indoles), 4099 (oxindole), 5873 (1991); 33 903, 3687 (serial cyclization), 6603, 7031 (1992); 35 3985 (tetrahydrofuran), 3995, 5161, 6221 (2-alkoxytetrahydrofurans) (1994); 36 3531 (1995) (2-alkoxytetrahydrofuran)</p> <p>CL 1725 (1985)</p> <p>JCS Perkin I 1351 (1986) (2-alkoxytetrahydrofurans)</p> <p>SL 201 (1990) (tetrahydrofuran); 228, 257 (1994) (both siloxane); 366 (1994) (tetrahydrofuran)</p> <p>JACS 94 6059, 6064 (1972); 105 3741 (1983) (2-alkoxytetrahydrofurans and -pyrans); 108 5893 (1986); 113 5791 (1991); 114 9688 (1992) (serial cyclization)</p> <p>CC 472 (1974)</p> <p>JCS Perkin II 795 (1975)</p> <p>Tetr 31 1737 (1975); 37 3073 (1981)</p> <p>JOC 43 6 (1978); 49 2298 (1984) (siloxanes); 52 4072 (1987); 53 2396, 3210 (1988); 54 5073 (1989); 57 4802 (1992); 59 3927, 3933, 4048 (1994) (all serial cyclizations)</p> <p>TL 22 2811 (1981) (rates, stereochemistry); 26 6001 (1985) (dihydrobenzofurans and -pyrans); 27 4525, 4529 (1986); 28 2637 (1987) (carbamens and carbacephams); 29 3691 (1988) (tetrahydrofurans and -pyrans); 30 2407 (1989); 31 4601 (1990); 33 2977, 7857 (bicyclic ketal) (1992); 36 2273 (serial cyclization), 4857 (1995)</p> <p>CC 85 (lactones), 464 (1986); 1456 (1987) (bicyclic alkane)</p> <p>SL 357 (1993) (serial cyclization)</p> <p>JOC 58 3877 (1993)</p>
	5, 6	
	5-7	

	6	JOC 41 3261 (1976); 53 3218 (1988); 58 4293 (1993); 59 2687, 3459, 6448 (1994) TL 26 4413 (1985); 28 1035 (1987); 29 4963 (1988) (tetrahydropyran); 30 4943 (1989); 31 1531, 2315, 5397 (lactams) (1990); 35 3703 (1994) CC 1438 (1987) (lactone, 2-alkoxytetrahydropyran) JACS 116 11335 (1994)
	6, 7	JOC 48 1841 (1983) (bicyclic β -lactams); 57 403 (1992) TL 32 2829 (1991) (<i>N</i> -heterocycles, <i>n</i> -Bu ₃ SnCl-NaBH ₃ CN) SL 165 (1991); 943 (1995)
	7	CC 472 (1974) TL 34 7317 (1993) JOC 58 4473 (1993)
	9	TL 36 4897 (1995)
	10, 14, 18	JACS 108 2787 (1986) (ketones)
	5	JOC 58 2894 (1993)
	5	JACS 109 609 (1987); 111 296, 1759 (1989) JOC 53 4522 (1988); 59 7661 (1994) (butyrolactone)
	6	TL 26 5675 (1985) JOC 52 1568 (1987)
SR	5	JACS 106 8209 (1984) (pyrrolizidinones); 110 5064 (1988) TL 29 897 (1988); 35 5837, 5841 (1994)
	5, 6	JACS 104 1430 (1982); 106 8201 (1984) (both pyrrolizidinones and indolizidinones) TL 31 759 (1990) (pyrrolidines and piperidines); 32 1491 (1991) (tetrahydrofurans and -pyrans)
	6	JOC 53 2683 (1988)
	6, 7	JACS 113 2335 (1991) (cyclic ethers)
	7	JOC 48 1841 (1983) (bicyclic β -lactams)
SePh	5	CC 307 (1983) (butyrolactones); 1205 (1985) (butyrolactones); 588 (1986) TL 26 6431 (1985); 28 2637 (1987) (carbapenam); 30 6307, 6311 (1989) JACS 110 5064 (1988) JOC 54 1997 (1989); 55 1786 (1990); 58 6857 (1993); 59 1396 (1994); 60 2607, 3518 (1995) SL 687 (1990); 285 (1992); 330 (1994) (all tetrahydrofurans)
	5, 6	JACS 106 8201 (1984) (pyrrolizidinones, indolizidinones); 117 3674 (1995) CC 353 (1987)

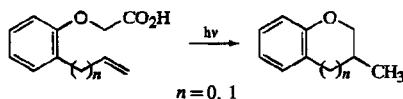
X	Ring size	
SePh (<i>continued</i>)	5, 6 (<i>continued</i>)	SL 257 (1990) JOC 56 5245 (1991); 58 7718 (1993) (tetrahydrofurans and -pyrans)
	6	JOC 53 2683 (1988) TL 30 2611 (1989) JACS 113 2335 (1991) (tetrapyrans)
	7	JOC 48 1841 (1983) (bicyclic β -lactams)
	9	SL 522 (1993)
NO ₂	5	CL 635 (1985) (tetrahydrofurans) Tetr 41 4013 (1985) (tetrahydrofurans)



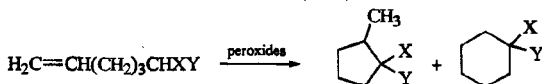
Reagent	X	Ring size	
(Me ₃ Si) ₃ SiH, AIBN	Br	5	TL 30 681 (1989) SL 366 (1994) (tetrahydrofuran)
NaBH ₃ CN, cat <i>n</i> -Bu ₃ SnCl	Br	5	TL 36 1127 (1995) (2-alkoxytetrahydrofuran)
distannane polymer, <i>i</i> -PrOH, hv	Br	5	SL 286 (1993) (butyrolactone)
		6	SL 28 (1993)
SmI ₂	Br	5	SL 803 (1993)
			TL 35 3995 (1994)
	SO ₂ Ph	9	SL 420 (1994)



SL 531 (1994)
TL 36 4429 (1995)

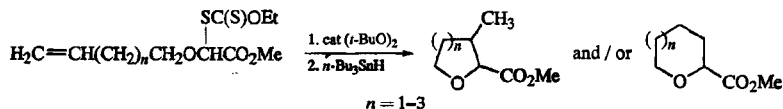


TL 36 1337 (1995)

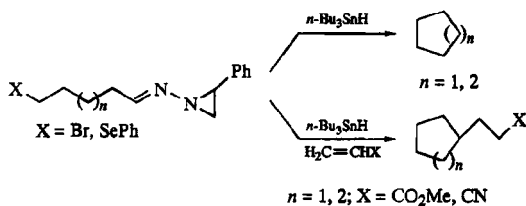


X, Y = H, H; H, COMe; H, CO₂Et; H, CN; COMe, CO₂Et; CO₂Et, CO₂Et; CO₂Et, CN

Acct Chem Res 4 386 (1971)
Org Syn Coll Vol 6 586 (1988)

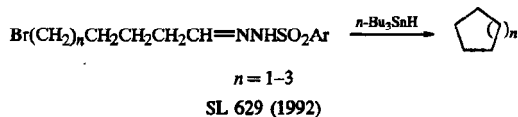


JOC 59 6671 (1994)

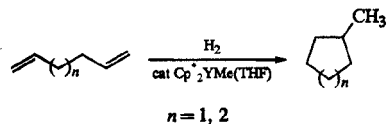


JACS 113 9882 (1991)

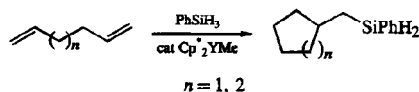
TL 36 6069 (1995)



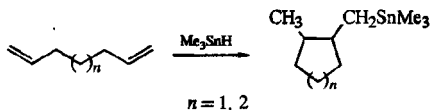
SL 629 (1992)



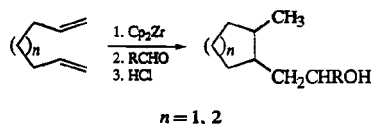
JACS 114 3123 (1992)



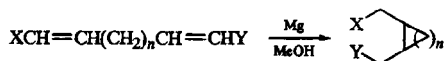
JACS 117 4415 (1995)



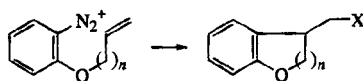
JACS 114 3115 (1992)



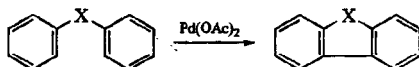
TL 35 695 (1994)


 $n = 1$ (X, Y = CO₂R, CO₂R); 3 (X, Y = CO₂R, CO₂R; CO₂R, CN; CN, CN)

TL 36 2281 (1995)



<u>n</u>	<u>X</u>	<u>Reagent(s)</u>	
1	Cl, Br, CN, SR	CuCl ₂ , CuBr ₂ , CuCN or RS ⁻	JACS 108 5890 (1986)
	I	NaI	JOC 52 1922 (1987)
2	I	NaI	JOC 52 2568 (1987)



<u>X</u>	
CO	JOC 40 1365 (1975) Syn 607 (1978) (3-aryolindole) TL 34 8361 (1993) (3-aryolindole)
CONH	JOC 40 1365 (1975) TL 30 5807 (1989)
O	JOC 40 1365 (1975) JCS Perkin I 1236 (1976); 1605 (1982)
NR	JOC 40 1365 (1975)



<u>X</u>	<u>Reagent(s)</u>	<u>Y</u>	
Br, I	Pd catalyst, base	CO ₂	TL 30 5249 (1989); 31 643, 6313 (1990); 33 4045 (1992) JACS 114 3568 (1992)
		C—C	SL 423 (1994) TL 36 6037 (1995)
		CONR	TL 34 5449 (1993)
		O	Syn 234 (1983)
		various groups	TL 32 3317 (1991)
	<i>n</i> -Bu ₃ SnH	CH ₂ CH ₂	TL 32 529 (1981)
		COCH ₂ , R ₂ NC=CH	TL 29 2987 (1988)
		CH ₂ NH	TL 31 1881 (1990)
	Δ, K ₂ CO ₃ , (PhCH ₂ NEt ₃)Cl	CONR	TL 32 65 (1991)
OTf	cat PdCl ₂ (PPh ₃) ₂ , <i>i</i> - BuCO ₂ Na, <i>i</i> -Pr ₂ NEt	CO ₂	TL 35 4591 (1994)

For Y = CH=CH, see page 196, Section 5.

6. Carbocationic Cyclization

Reviews:

Acct Chem Res 1 1 (1968); 8 152 (1975)

Bioorg Chem 5 51 (1976)

Angew 88 33 (1976)

P. A. Bartlett in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, p 341

Some recent references:

JACS 103 4615 (1981); 104 3508 (1982); 107 522, 2712 (1985) (both Hg promoted); 109 2517, 5852 (1987); 115 493, 497, 504, 515 (1993)

JOC 46 2709 (1981); 50 3988 (1985); 52 4878 (1987) (Hg promoted); 54 4731 (1989); 55 5078 (1990); 57 955, 4598 (1992); 58 7918 (1993); 59 2324, 6150 (1994); 60 5726 (cationic and Hg) (1995)

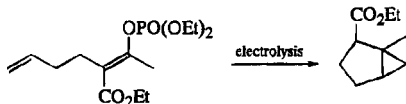
JCS Perkin I 2956 (1981)

J Chem Res (S) 20 (1981)

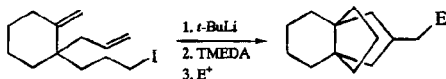
TL 28 4053 (Sn promoted), 6413 (Hg promoted) (1987); 30 3023 (Hg promoted), 6299, 6303 (both vinylic Si trap) (1989); 33 1679 (Hg promoted) (1992); 34 7849 (1993); 35 1469, 1503, 5693 (Hg promoted), 9141, 9685 (1994)

SL 169 (1995) (Hg promoted)

7. Polycyclics



JACS 111 739 (1989)

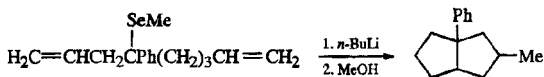


$E^+ = H^+, RX, RCHO, R_2CO, DMF, CO_2, Me_3SiCl, I_2$

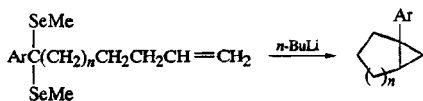
JACS 111 765 (1989); 114 8053 (1992)

TL 31 5993 (1990)

JOC 55 6058 (1990)

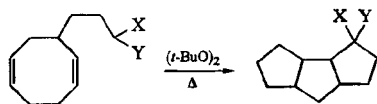


TL 32 417 (1991)



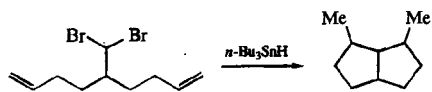
$n = 1, 2$

TL 32 417 (1991)



X, Y = CN, CO₂Et; SCH₂CH₂S

JACS 108 1708 (1986)



IOC 55 3440 (1990)

5. AROMATIZATION

1. Dehydrogenation

Reviews:

"Newer Methods of Preparative Organic Chemistry," Vol 1 (1963) (S, Se, Pt)

"The Chemistry of the Quinoid Compounds," Ed. S. Patai, J. Wiley (1974), Chpt 7

Houben-Weyl, Vol V/2b, p 107



Review: Chem Rev 78 317 (1978)

cat $[\text{Ni}_3(\text{PO}_4)_2 + \text{H}_2]$

CL 967 (1976)

cat $\text{Ni-Al}_2\text{O}_3$, C_6H_6

JACS 63 1320 (1941)

cat $\text{Ni-Cr}_2\text{O}_3$, C_6H_6

JACS 63 1320 (1941); 71 2962 (1949)

cat $\text{Ni-Cr}_2\text{O}_3$, C_6H_6 , PhSPh or thiophene

JACS 70 381 (1948)

cat Pd-asbestos

JCS 583 (1957)

cat Pd-C

JCS 583 (1957)

Helv 51 1102 (1968); 52 1023 (1969)

cat Pd, C_6H_6

JACS 71 2962 (1949)

cat Pt-C

JCS 583 (1957)

cat Pt, C_6H_6

JACS 63 1320 (1941); 71 2955, 2962 (1949)

S

JCS 1832 (1932)

Tetr 30 3303 (1974)

Se

JCS 1431 (1936)



Review: Chem Rev 78 317 (1978)

cat C	SL 539 (1990)
cat Pd-C	JACS 90 6992 (1968)
cat Pt-alumina	Ann 670 23 (1963) TL 3491 (1973)
S	JCS 1832 (1932) JACS 60 940 (1938) JOC 38 1430 (1973)
Se	Ber 1471 (1933)
SeO ₂ , trimethylsilyl polyphosphate	TL 33 6363 (1992)
quinones	Adv Org Chem 2 329 (1960) (review)
DDQ	JOC 60 3448 (1995)
tetrachlorobenzoquinone	JACS 61 1407 (1939); 62 983 (1940) BCSJ 44 2841 (1971)



Review: Chem Rev 78 317 (1978)

cat Ni-Al ₂ O ₃ , C ₆ H ₆	JACS 63 1320 (1941)
cat Pd-C	Ber 96 707 (1963) Syn 307 (1971) JOC 55 3787 (1990)
cat Pd, C ₆ H ₆	JACS 71 2962 (1949)
cat Pt, C ₆ H ₆	JACS 71 2955 (1949)
S	Helv 10 915 (1927) Ber 65 883 (1932) JCS 1286 (1938)
Se	Ber 60 2323 (1927) JCS 1125 (1932); 1012 (1933); 365 (1934); 62 (1936); 1845 (1959)
(<i>i</i> -AmS) ₂	JACS 59 2351 (1937)
tetrachlorobenzoquinone	JACS 61 1407 (1939)
DDQ	JCS 3569 (1954) Chem Rev 67 153 (1967) (review) JACS 110 8483 (1988) JOC 55 3158 (1990)
Ph ₃ COH, CF ₃ CO ₂ H	TL 3217 (1974)



2,4,6-(NO ₂) ₃ C ₆ H ₂ NNPh ₂	JCS 3574 (1954)
SeO ₂ , trimethylsilyl polyphosphate	TL 33 6363 (1992)
O ₂ , cat H ₅ PMo ₁₀ V ₂ O ₄₀ (tetraglyme) ₃	JOC 54 4607 (1989)



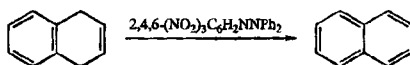
Review: Chem Rev 78 317 (1978)

cat Pd-C	TL 191 (1969)
quinones	Adv Org Chem 2 239 (1960) (review)
DDQ	JACS 107 5305 (1985) JOC 51 5100 (1986); 58 4979 (1993); 59 7056 (1994) SL 53 (1990)
(NC) ₂ C=C(CN) ₂	TL 205 (1962) JACS 85 3436 (1963); 87 2751 (1965); 102 886 (1980) JOC 53 3247 (1988)
2,4,6-(NO ₂) ₃ C ₆ H ₂ NNPh ₂	JCS 3574 (1954)
act MnO ₂	Syn Commun 12 637 (1982) JACS 110 4823 (1988)
O ₂ , cat H ₅ PMo ₁₀ V ₂ O ₄₀ (tetraglyme) ₃	JOC 54 4607 (1989)

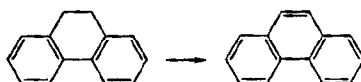


Review: Chem Rev 78 317 (1978)

cat Pd-C	Ann 686 40 (1965) JOC 53 4253 (1988)
cat Pt	JCS 1431 (1936)
cat Pt, C ₆ H ₆	JACS 71 2955 (1949)
S	JOC 23 797 (1958)
Se	JCS 62, 1431 (1936)
SeO ₂	Z Chem 13 216 (1973)
SeO ₂ , trimethylsilyl polyphosphate	TL 33 6363 (1992)
2,4,6-(NO ₂) ₃ C ₆ H ₂ NNPh ₂	JCS 3574 (1954)
tetrachlorobenzoquinone	Ann 686 40 (1965) JOC 54 3533 (1989)
DDQ	JOC 52 2226, 3205 (1987); 54 3800, 5272 (1989); 56 3501 (1991)
O ₂ , cat H ₅ PMo ₁₀ V ₂ O ₄₀ (tetraglyme) ₃	JOC 54 4607 (1989)



JCS 3574 (1954)



Review: Chem Rev 78 317 (1978)

cat Pd-C

JOC 58 4155 (1993)

(Ph₃C)ClO₄

JCS 2773 (1959)

Ph₃COH, CF₃CO₂H

TL 3217 (1974)

n-BuLi

JACS 95 2376 (1973); 96 2434 (1974)

DDQ

JOC 52 3196 (1987); 57 3746 (1992); 58 4155 (1993)

JACS 113 183 (1991)



Review: Chem Rev 78 317 (1978)

cat Pd-C

Ber 96 707 (1963)

Cu

Ber 72 1817 (1939); 96 707 (1963)

SeO₂

JCS 764 (1947)

tetrachlorobenzoquinone

JACS 61 1407 (1939)

Ber 96 707 (1963)

DDQ

JOC 52 3205 (1987)

TL 35 4493 (1994)

2,4,6-(NO₂)₃C₆H₂NNPh₂

JCS 3574 (1954)

(Ph₃C)ClO₄

JCS 2773 (1959)

Ph₃COH, CF₃CO₂H

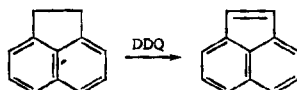
TL 3217 (1974)

PhSO₃H, PhNO₂

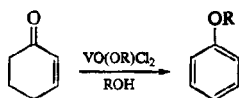
Ber 91 2109 (1958)

n-BuLi / CdCl₂

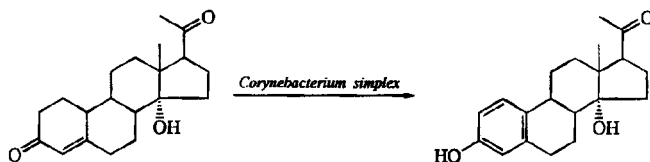
JACS 95 2376 (1973); 96 2434 (1974)



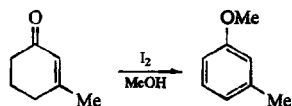
JOC 52 3205 (1987); 55 3787 (1990)



JOC 55 358 (1990)

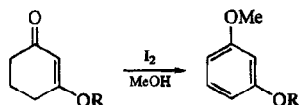


JOC 27 361 (1962); 54 3984 (1989)

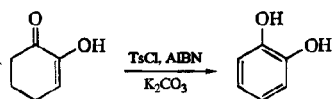


Chem Ind 888 (1980)

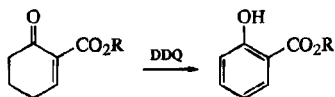
TL 31 481 (1990)



TL 32 3441 (1991)

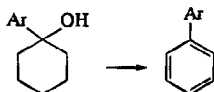


TL 29 73 (1988)



TL 31 3421 (1990)

2. Elimination

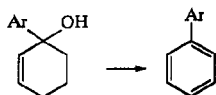


JCS 1832 (1932)

JOC 30 2942 (1965)

S

DDQ

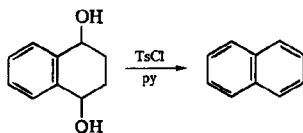


DDQ

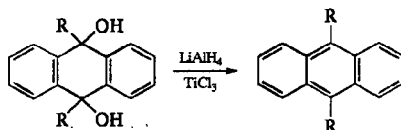
JOC 28 2403 (1963)

 Ph_3COH , $\text{CF}_3\text{CO}_2\text{H}$

TL 3217 (1974)

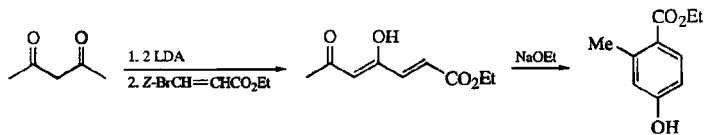


JOC 53 6106 (1988)

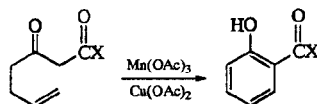


JOC 54 850 (1989)

See also page 193, Section 3.



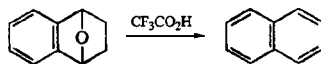
TL 26 4419 (1985)



X = R, OR

TL 28 845, 6109 (1987)

JOC 58 3185 (1993)



TL 36 4181 (1995)

 Me_3SiCl , NaI

JOC 54 5667 (1989)

TL 34 8333 (1993)

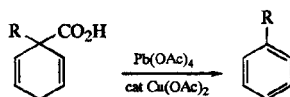
LiAlH₄, TiCl₄, Et₃N

JOC 47 140 (1982); 55 3214 (1990); 58 3118, 7498 (1993)

JACS 110 462 (1988); 115 11604 (1993)

n-BuLi; TiCl₃, FeCl₃ or WCl₆

JOC 46 1251 (1981)

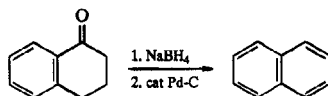


JCS 1551 (1950)

Ber 94 2095 (1961)

TL 2079 (1976); 27 3923 (1986)

3. Reductive Elimination



JOC 58 4155 (1993)

NaBH₄, MeOH, diglyme

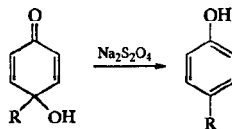
TL 35 1131 (1994)

NaBH₄, *i*-PrOH

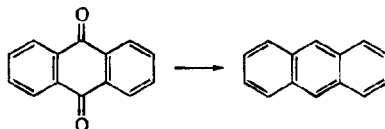
JOC 39 770 (1974)

NaBH₄, CF₃CO₂H

Syn 763 (1978)



JOC 57 5547 (1992)



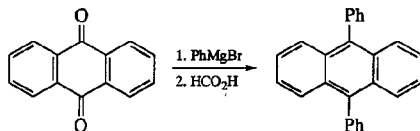
HI, HOAc

JOC 43 3423 (1978); 44 4813 (1979); 52 3205 (1987)

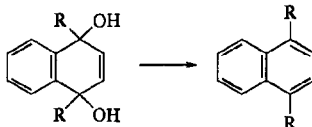
HI, HOAc, P

Org Syn Coll Vol 7 18 (1990)

Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$	JACS 113 5775 (1991)
Ph_2SiH_2 , Δ	JOC 26 4817 (1961)
NaBH_4 , EtOH or <i>i</i> -PrOH	JACS 113 5775 (1991)
$\text{NaBH}_4/\text{HCl}/\text{NaBH}_4$	JOC 39 770 (1974)
NaBH_4 , $\text{BF}_3 \cdot \text{OEt}_2$ or AlCl_3	Ind J Chem 1 19 (1963)
Zn , H_2O , NH_3	J Prakt Chem 23 137 (1881) JACS 94 3080 (1972); 112 2577 (1990); 114 9309 (1992)
Zn , CuSO_4 , NH_3 , H_2O	JACS 114 9877 (1992)
Zn , py / HOAc / HCl	Syn Commun 7 161 (1977)



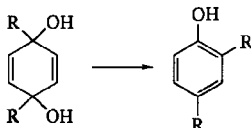
JACS 112 2577 (1990)



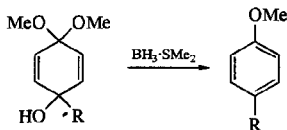
HI TL 29 1359 (1988)

 SnCl_2 , HCl JOC 55 3787 (1990)

See also page 191, Section 2.



HOAc TL 29 4827 (1988)

HI TL 29 4827 (1988)
JACS 116 5089 (1994)

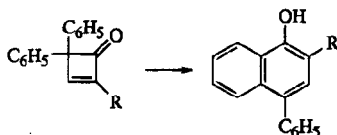
JACS 113 8516 (1991)



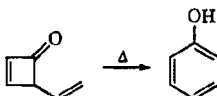
See page 191, Section 2.

4. Rearrangement

See also page 207, Section 6.



Angew Int 14 500 (1975)

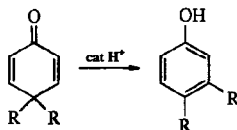


JOC 51 3065 (1986); 53 996, 4166 (1988); 54 2032, 4024 (1989); 55 1177 (1990); 57 326 (1992); 58 3550, 3942 (1993); 59 3284, 7572 (1994); 60 644, 8194 (1995)

Heterocycles 27 1191 (1988)

Tetr 45 3053 (1989)

JACS 112 1897 (1990); 114 1412 (1992); 115 6101, 9868 (1993)



JACS 68 1712, 1715 (1946)

Advances in Alicyclic Chemistry 1 129 (1966) (review)

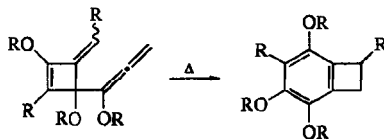
H. J. Shine, "Aromatic Rearrangements," Elsevier, New York (1967), pp 55-66 (review)

B. Miller in "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, Wiley Interscience, New York (1968), Vol 1, pp 247-313 (review)

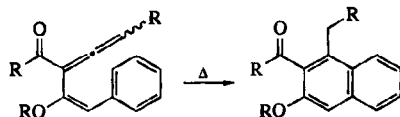
M. J. Perkins, P. Ward in "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, Wiley Interscience, New York (1971), Vol 4, pp 55-112 (review)

Acct Chem Res 8 245 (1975) (review)

JOC 59 1831 (1994)

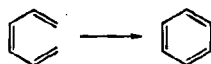


TL 34 6177 (1993)



JOC 60 3274 (1995)

5. Cyclization and Annulation



cat Pd-C

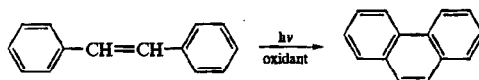
JOC 60 1939 (1995)

S

JACS 115 3511 (1993)

DDQ

JACS 115 3511 (1993)



Chem Rev 76 509 (1976) (review)

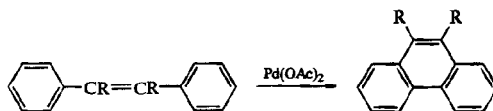
Org Rxs 30 1 (1984) (review)

JOC 53 4447 (1988); 54 3091, 4105 (1989); 55 4478 (1990); 56 3769, 6787 (1991); 58 4155 (1993); 60 1658, 4905, 6123, 8101 (1995)

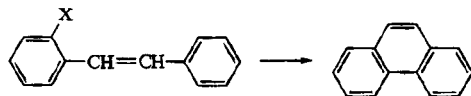
JACS 111 4522 (1989); 113 8993 (1991); 115 3182, 3199, 10791 (1993)

TL 32 6831 (1991); 33 5563 (1992)

SL 521 (1992)



TL 34 8361 (1993) (indoles)

XReagent(s)

Cl

A

TL 35 801 (1994)

Br

hv, Et₃N

TL 29 2987 (1988); 36 935 (1995)

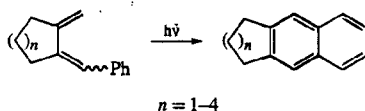
n-Bu₃SnH

JOC 60 6114 (1995)

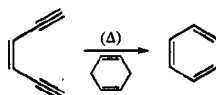
JOC 60 6114 (1995)

TL 36 935 (1995)

OMe	$h\nu, H^+$	JOC 54 4619 (1989)
N_2^+	$\Delta, (Cu)$	Chem Rev 56 27 (1956); 76 509 (1976) (reviews)
	electrolysis	Org Rxs 9 410 (1957) (review)
	Cu	JOC 36 1769 (1971)
	Br^- , (Hg)	JOC 36 1769 (1971)
	I^-	JOC 36 1769 (1971)
	$K_2Fe(CN)_6 \cdot 3H_2O$	Austral J Chem 22 993 (1969); 23 2503 (1970)
	cat ferrocene	JOC 36 1769 (1971)
		JOC 60 196 (1995)
		JOC 60 196 (1995)



JOC 56 989 (1990)



CC 1516 (1971)

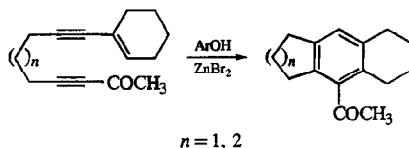
Acct Chem Res 6 25 (1973) (review)

TL 21 217 (1980); 31 185 (1990); 33 3277, 7511 (1992); 36 6607 (1995)

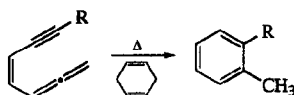
JACS 110 4866 (1988); 114 2544, 2560, 7360, 8890, 8908, 9279 (1992); 115 11618, 11744 (1993)

Angew Int 30 1387 (1991) (review)

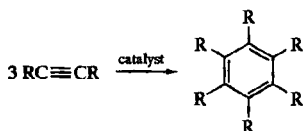
JOC 58 5422, 6556, 6559 (1993); 59 5038, 5114, 5833, 7876 (1994)



JOC 59 5514 (1994)



TL 30 4995 (1989)



/S:

Russ Chem Rev 35 510 (1966); 43 48 (1974)

Acct Chem Res 10 1 (1977)

JOC 52 1161 (1987)

i-Bu₂AlH, Δ

JACS 88 2213 (1966)

R₃Al (R = Et, *i*-Bu), TiCl₄

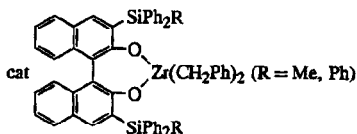
JACS 81 1514 (1959)

JOC 26 2234 (1961)

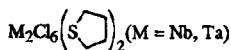
Helv 48 509 (1965)

Me₃SiCl, cat Pd-C

JOC 52 1161 (1987)



JACS 117 3008 (1995)



Macromolecules 14 235 (1981)

R₃Cr

JACS 81 6090, 6203 (1959)

JOMC 5 176 (1966)

Fe

JOMC 249 195 (1983)

Fe₃(CO)₁₂

Ber 93 103 (1960)

CpCo(CO)₂

Angew Int 14 712 (1975); 23 539 (1984)

Acct Chem Res 10 1 (1977) (review)

JACS 99 4058 (1977); 107 1379, 5670 (1985); 108

836, 3150 (1986); 114 9713 (1992)

CC 953 (1982)

TL 30 2541 (1989); 35 417 (1994)

SL 667 (1990); 971 (1992)

JOC 58 4298 (1993); 60 2664 (1995)

Co₂(CO)₈

Ber 93 103 (1960); 94 2817 (1961)

JACS 86 4729 (1964)

Hg[Co(CO)₄]₂

Ber 93 103 (1960); 94 2829 (1961)

Helv 48 509 (1965)

Co carbonyl alkyne complexes

Ber 93 103 (1960); 94 2817, 2829 (1961)

ClRh(PPh₃)₃

TL 23 2691 (1982); 29 813 (1988)

JCS Perkin I 1357 (1988)

JACS 117 6605 (1995)

$\text{Rh}_2[\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3]_4$

TL 35 9139 (1994)

 $\text{Ni}(\text{CO})_2(\text{PPh}_3)_2$

Ann 560 104 (1948)

JCS 69 (1950)

JOC 26 5155, 5169 (1961)

 $\text{Ni}(\text{PPh}_3)_4$

JCS Perkin I 2603 (1990); 2163 (1992)

CC 277 (1991)

JOC 59 6133 (1994)

 $\text{Ni}(\text{COD})_2$, chiral diphosphine

JOC 59 6133 (1994) (chiral)

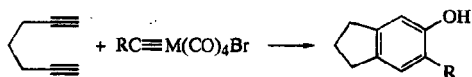
 $\text{Ni}(\text{H}_2\text{C}=\text{CHCN})_2$

Ber 94 1403 (1961)

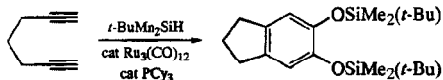
 $\text{PdCl}_2(\text{PhCN})_2$

JACS 84 2329 (1962); 92 2276 (1970)

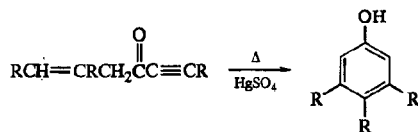
Can J Chem 43 470 (1965)

 $\text{M} = \text{W}, \text{Cr}$

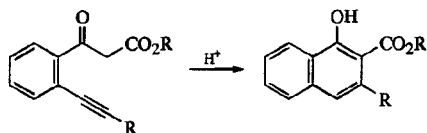
TL 26 2159 (1985)



JACS 115 11614 (1993)



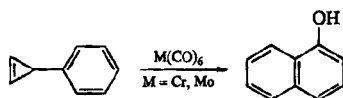
TL 32 1279 (1991)



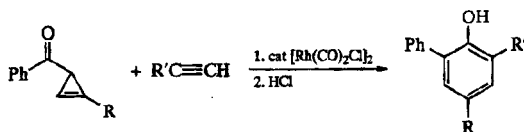
TL 35 1127 (1994)



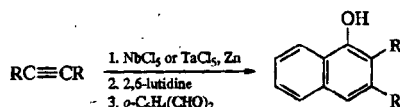
JOC 55 1611 (1990)



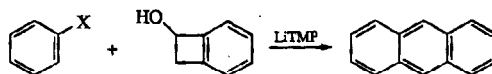
JACS 109 4397 (1987); 116 7108 (1994)



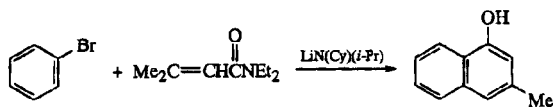
JACS 114 5881 (1992)



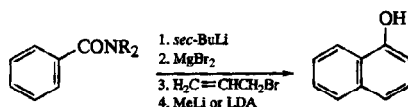
TL 31 369 (1990)



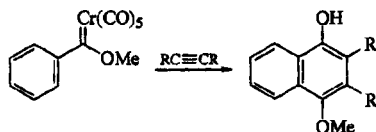
JOC 57 7122 (1992)



TL 35 8747 (1994)



JOC 51 271 (1986)



Angew Int 14 644 (1975)

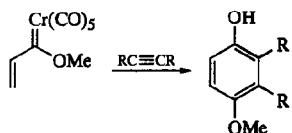
JACS 103 7677 (1981); 104 5850 (1982); 106 434, 7565 (1984); 110 2312 (1988); 116 7108, 10921 (1994)

Pure Appl Chem 55 1689 (1983) (review)

Organomet 7 2346 (1988)

TL 29 2513 (1988); 30 2037 (1989); 31 605, 609 (1990); 32 7759 (1991)

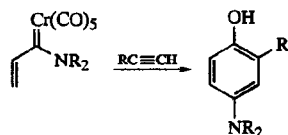
JOC 53 4166 (1988); 54 3625 (1989); 55 1919 (1990); 56 1666, 2115 (1991)



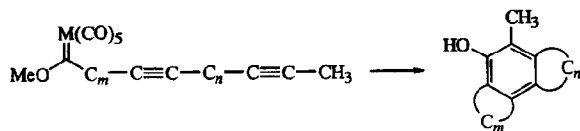
JOC 59 3047 (1994)

JACS 116 3113, 6449, 7449 (1994)

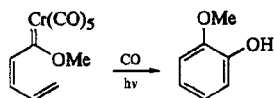
TL 36 1871 (1995)



JOC 60 4566 (1995)

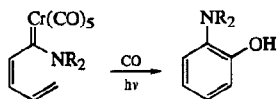
 $M = Cr, W$; $m = 3, 4$; $n = 2-4$

JACS 116 7616 (1994)

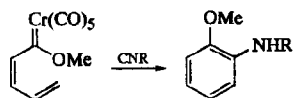


JACS 113 7418 (1991)

TL 34 7379 (1993)

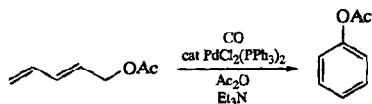


JOC 58 538 (1993)



JACS 114 8722 (1992)

TL 34 5401 (1993)

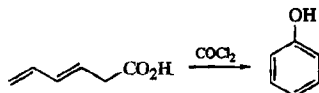


CC 575 (1987)

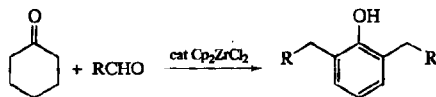
CL 1159 (1988)

JOC 53 3832 (1988); 56 1922 (1991) (heterocycles); 58 6818 (1993)

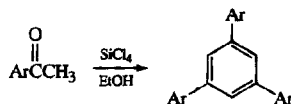
TL 30 95 (1989) (heterocycles)



JOC 59 2043 (1994)

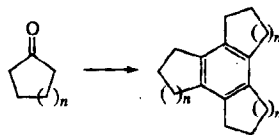


JOC 53 5181 (1988)



TL 32 4175 (1991); 33 821 (1992)

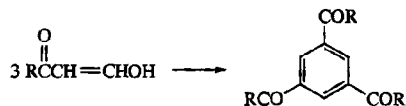
SL 405 (1993)

 $n = 1, 2$ SiCl_4 , EtOH

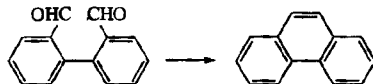
TL 32 4175 (1991); 33 821 (1992)

 ZrCl_4 or Cp_2ZrCl_2

JOC 56 2253 (1991)



JOC 53 5564 (1988)



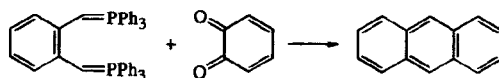
N_2H_2 , HOAc

JCS 1375 (1958)

TL 32 3025 (1991)

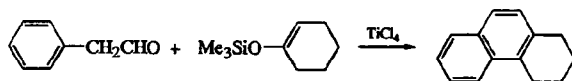
 $\text{TsNHNH}_2/\text{NaH}$ or $n\text{-BuLi}/(\text{CuI})$

TL 32 3025 (1991)

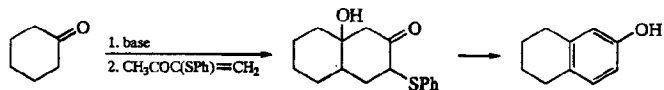


SL 799 (1992)

Tetr 48 3735 (1992)

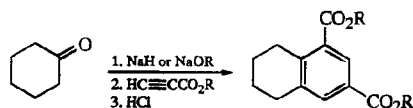


TL 29 3885 (1988)

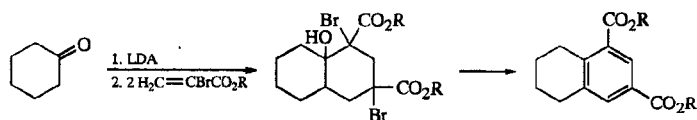


CC 1183 (1980)

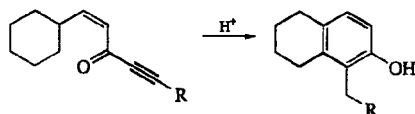
JOC 47 1200 (1982)



TL 30 3579 (1989)

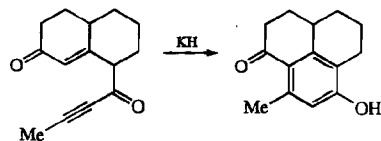


JACS 108 511 (1986)

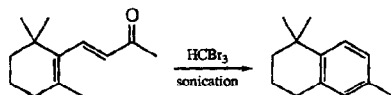


TL 29 6873 (1988)

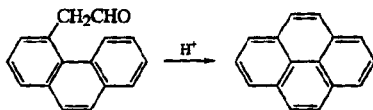
JOC 60 376 (1995)



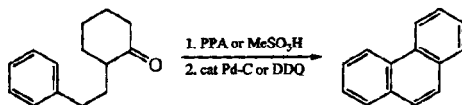
JACS 111 5472 (1989)



TL 35 7833 (1994)



TL 30 6603 (1989)

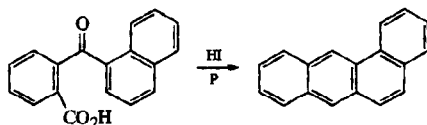


Can J Chem 45 2630 (1967)

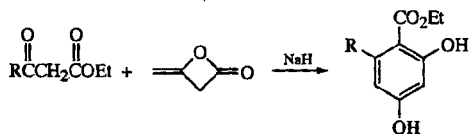
TL 29 3207 (1988)

JOC 56 1210 (1991)

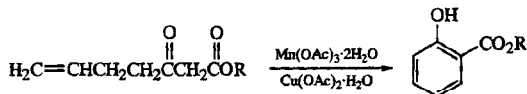
Tetr 48 3735 (1992)



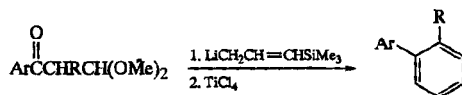
JOC 46 2601 (1981)



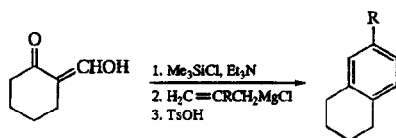
Chem Pharm Bull 20 1574 (1972); 30 2440, 2590 (1982)



JOC 54 38 (1989)



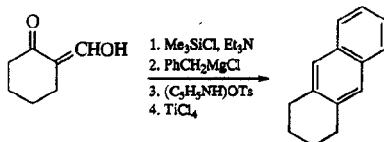
TL 22 3335 (1981)



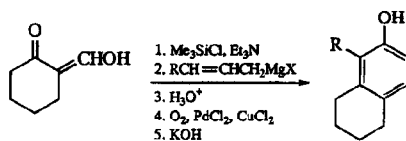
JOC 47 3163 (1982)

Syn 467 (1983)

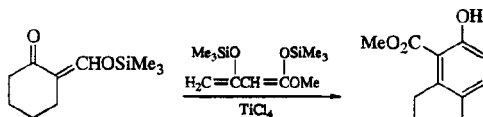
TL 27 4541 (1986)



TL 27 2571 (1986)



TL 23 2823 (1982)

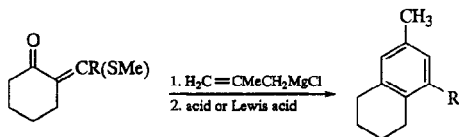


CC 578 (1979)

JACS 102 3534 (1980)

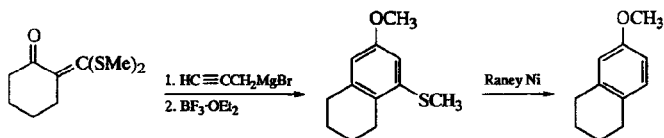
TL 23 2935 (1982)

JOC 53 1584 (1988)

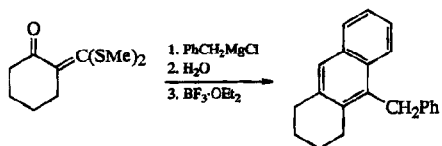


R = Me, SMe

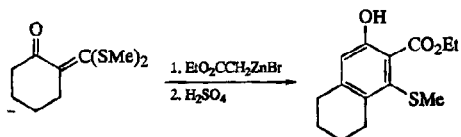
TL 25 5095 (1984); 26 39 (1985)



TL 28 1459 (1987)

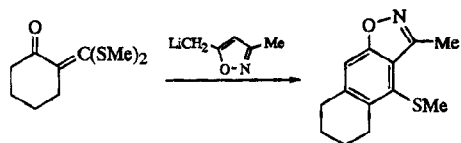


TL 27 117 (1986)

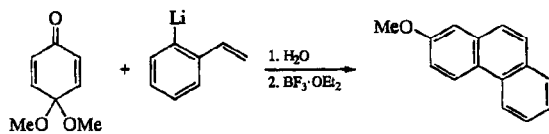


TL 29 497 (1988)

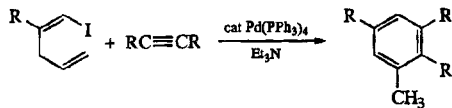
JOC 55 5589 (1990)



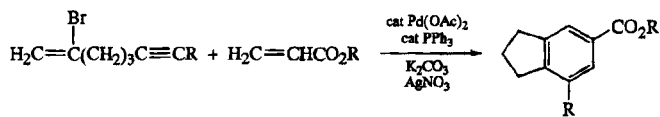
TL 29 501 (1988)



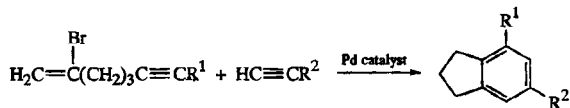
TL 33 2269 (1992)



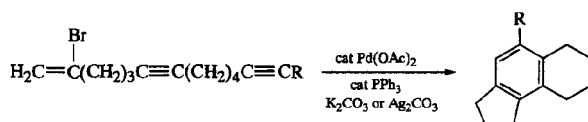
JACS 111 3454 (1989)



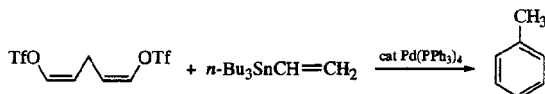
SL 865 (1992)



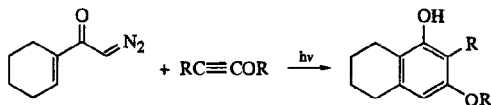
TL 32 4167 (1991); 33 3253 (1992)



SL 777 (1991)



TL 35 2465 (1994)

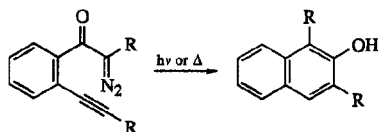


JACS 112 3093 (1990)

TL 31 1527 (1990)

SL 573 (1995)

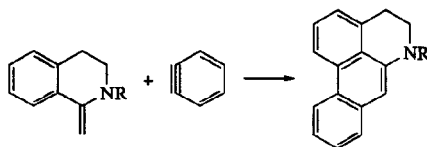
JOC 60 8341 (1995)



TL 32 5923 (1991)

JOC 58 6429 (1993)

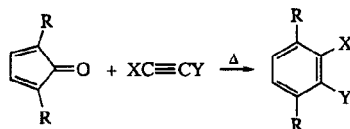
6. Diels–Alder and Related Reactions



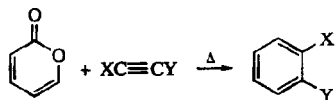
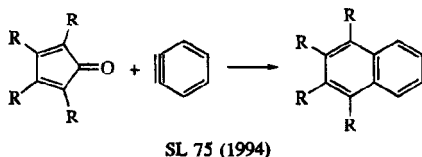
TL 23 457 (1982); 24 2107 (1983); 26 4559 (1985)

JOC 56 2984 (1991)

SL 903 (1992) (intramolecular)



JOC 52 496 (1987); 53 1687 (1988); 55 1937 (1990)



Ber 70 1354 (1937)

J Gen Chem USSR 29 3200 (1959)

JOC 29 2534 (1964); 42 2930 (1977); 47 1150 (1982)

JACS 89 952, 4793 (1967)

JOMC 34 119 (1972)

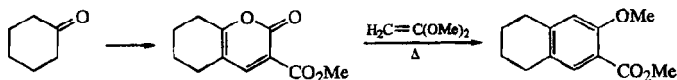
CC 95 (1978); 926 (1984) (hetaryne, pyridocarbazole)

TL 22 3355 (1981); 29 2693 (1988) (intramolecular, carbazoles)

Ann 914 (1982)

JCS Perkin I 2505 (1985) (carbazoles); 247 (hetaryne, pyridocarbazole), 1407 (carbazoles) (1988); 2463 (1989) (carbazoles)

SL 521 (1990)

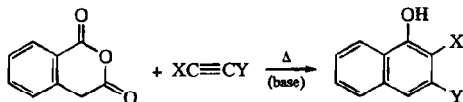


TL 23 4551, 4555, 4559 (1982); 24 4939 (1983)

JOC 49 4033, 4055 (1984)

Org Syn 65 98 (1987)

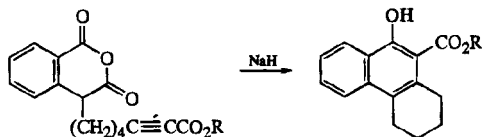
Org Syn Coll Vol 8 444 (1993)



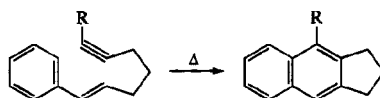
TL 22 4283 (1981); 25 309 (1984)

Chem Pharm Bull 31 2691 (1983); 33 4723 (1985)

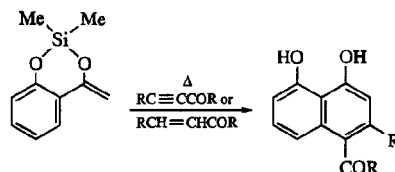
JOC 49 473 (1984); 56 119 (1991) (intramolecular)



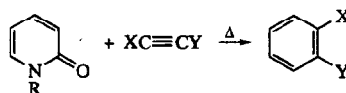
TL 29 5943 (1988)



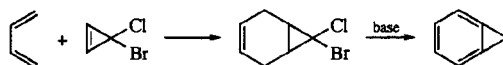
TL 30 829 (1989)



TL 25 1813 (1984); 30 3995 (1989) (intramolecular)



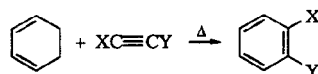
JCS Perkin I 169 (1982)



JACS 106 440 (1984); 113 4331 (1991)

JOC 53 1312 (1988)

Helv 73 1228 (1990)



Austral J Chem 22 2635 (1969)

Syn 223 (1982)

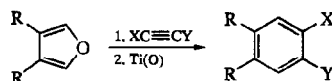
JACS 107 2712 (1985)

JCS Perkin I 1907 (1989)

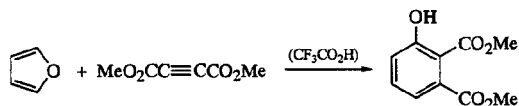
TL 33 4061 (1992); 34 2629 (1993); 36 5339 (1995)

JOC 60 560 (1995)

SL 981 (1995)

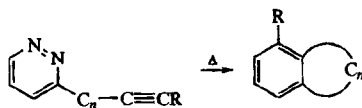
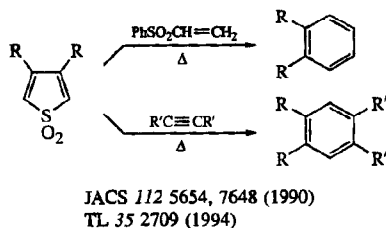
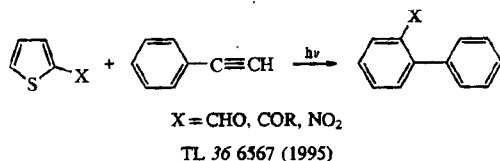
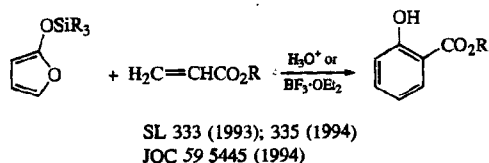
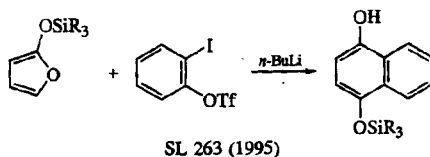
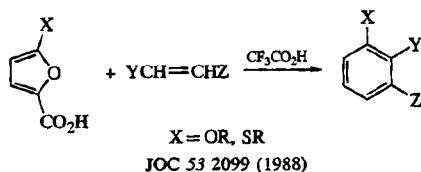


TL 36 8535 (1995)

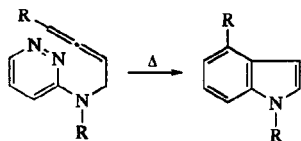


SL 333 (1993)

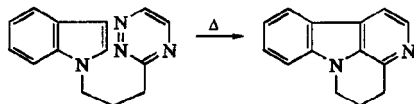
JOC 59 7353 (1994)



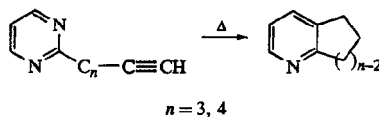
JOC 49 2240 (1984); 51 3250 (1986); 52 4280 (1987) (pyridines); 53 800 (pyridines), 3568 (lumazines) (1988); 54 4984 (1989) (pyridine); 56 1807 (1991) (pyridines)
Chem Zeitung 108 331 (1984) (pyridazines)
TL 26 2419 (pyridines), 4355 (pyridines, pyridazines) (1985); 27 431 (pyridines), 1967 (pyridines), 2107 (pyridines), 2747 (pyridines, pyridazines) (1986); 28 379 (1987) (pyridines)
JACS 109 2717 (1987)



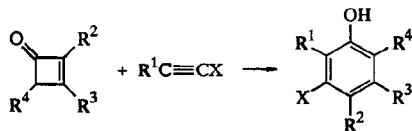
JACS 113 4230 (1991)



TL 36 6591 (1995)



JOC 57 3000 (1992)



JOC 49 1672 (1984)

JACS 108 806 (1986); 110 3693 (1988)

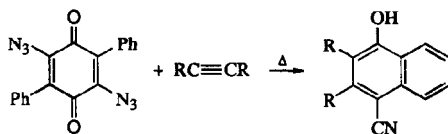
TL 29 4917 (1988)

indenyl-Co(PPh₃)₂

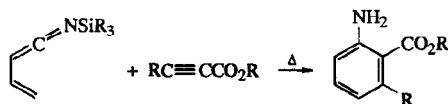
JACS 112 8617 (1990)

cat Ni(COD)₂

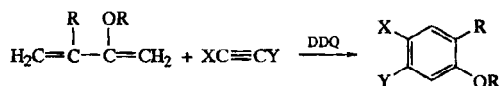
JACS 113 2771 (1991)



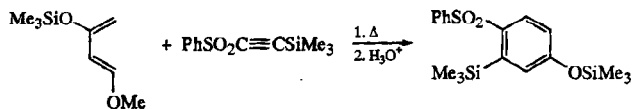
TL 28 5013 (1987)



TL 28 397 (1987)

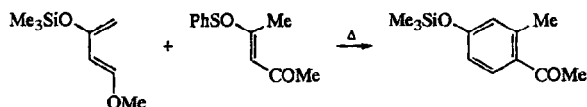


JOC 60 6025 (1995)

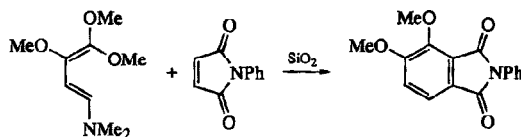


JACS 96 7807 (1974); IOI 7001 (1979)

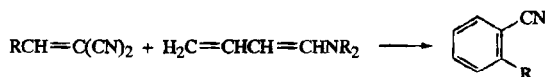
JOC 46 1951 (1981)



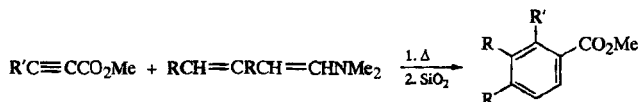
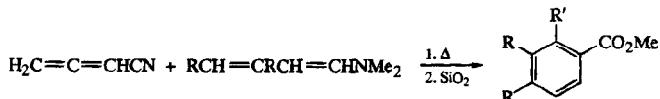
JACS 101 7008 (1979)



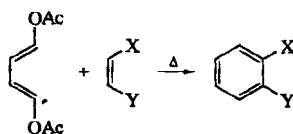
Syn 649 (1981)



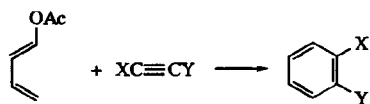
JOC 55 2545 (1990)



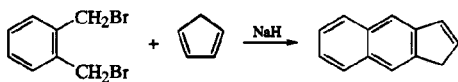
JOC 59 4844 (1994)



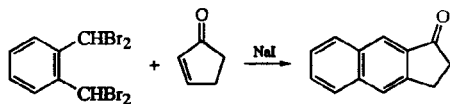
TL 1157 (1964)



JOC 58 7149 (1993)



SL 642 (1991)



SL 642 (1991)

JOC 59 6484 (1994)

ALKENES

GENERAL REFERENCES

"The Chemistry of Alkenes," Ed. S. Patai, Interscience, New York (1964)

F. Asinger, "Olefins," Pergamon Press, New York (1966)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/1c (dienes), G. Thieme, Stuttgart (1970)

Quart Rev 25 135 (1971)

Syn 175 (1971)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/1b (alkenes, cycloalkenes, aryl alkenes), G. Thieme, Stuttgart (1972)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/1d (polyenes), G. Thieme, Stuttgart (1972)

Chem Rev 89 1067-1160 (1989) (strained alkenes)

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E/17d (cyclopropenes), G. Thieme, Stuttgart-New York (1997)

1. ISOMERIZATION OF ALKENES

Review: Syn 405 (1970)

For reactions of allylic organometallics that proceed with allylic transposition, see page 351, Section 5.

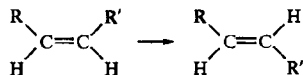
1. Alkene Inversion

See also page 251, Section 2, for elimination via diols, epoxides, β -dihalides, β -halo esters and bromohydrins.

Reviews:

Chem Rev 55 625 (1955)

Tetr 36 557 (1980)



h ν

JACS 107 1034 (1985); 110 189 (1988)

h ν , (PhS) $_2$

JCS C 260 (1966)

JACS 89 2758 (1967); 114 1084 (1992)

Helv 51 548 (1968)

Org Syn 63 192 (1984)

TL 28 47, 6437 (1987); 30 3243 (1989)

PhSH, AIBN

JOC 51 260 (1986) (R = 3° alkyl); 52 4674 (1987)

(Me $_3$ Si) $_3$ SiH, AIBN

TL 34 5147 (1993)

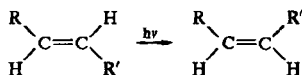
JOC 60 3826 (1995)

cat Ph $_3$ GeH, cat BEt $_3$

TL 28 3709 (1987)

KI, HOAc (enone)

JACS 111 6648 (1989)



Helv 38 1338 (1955)

JACS 79 2318 (1957); 86 2087 (1964); 107 1034 (1985); 108 3005 (R = Ph, R' = CO₂R; added BF₃·OEt₂ or EtAlCl₂), 3016 (R = alkyl, R' = CO₂R; added EtAlCl₂) (1986); 111 6648 (1989)

JOC 38 1247 (1973)

Tetr 31 193 (1975)

2. Simple Rearrangement

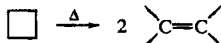
2.1. Thermal

Reviews:

"Molecular Rearrangements," J. Wiley and Sons, New York (1963), Vol 1, Chpt 11
Angew Int 2 115 (1963)



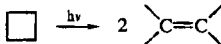
See page 547, Section 3.



JACS 83 3935, 4884 (1951)

2.2. Photochemical

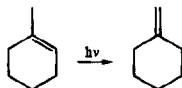
See also page 219, Section 1 (Alkene Inversion).



CC 490 (1978); 462 (1983)

JACS 102 5265 (1980)

CL 1855 (1985)



JACS 89 5199 (1967)



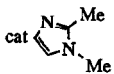
X
R

Reagent

—

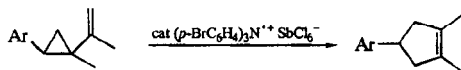
Helv 46 678 (1963)

TL 1203 (1964)

		Pure Appl Chem 9 481 (1964) BSCF 1185 (1973) Can J Chem 54 2127 (1976) JACS 109 2479 (1987); 111 8756 (1989) (acid catalysis)
OH	—	JACS 85 1210 (1963) (dienoic acid → allenic acid) Pure Appl Chem 9 481 (1964) JOC 33 1671 (1968)
OR	—	Pure Appl Chem 9 481 (1964) CC 137 (1965) JOC 32 3222 (1967); 33 1671 (1968); 34 609 (1969); 38 2558 (1973) TL 4987, 4991 (1968); 489 (1970); 33 6073 (1992) JACS 91 198 (1969); 93 5490 (1971) J Photochem 1 433 (1972/73) BCSJ 46 2181 (1973) (lactone) Syn 1019 (1983) (lactones)
		TL 24 4299 (1983); 27 5555 (1986) Can J Chem 62 1933 (1984) JOC 50 873 (1985) SL 729 (1994)
	Et ₂ NH ephedrine (enantioselective)	TL 26 4945 (lactones), 6079 (1985); 27 2997, 3001 (1986) Pure Appl Chem 58 1257 (1986) (esters and lactones) JACS 110 4824 (1988); 112 9263 (1990) Tetr 45 6171 (1989) (esters and lactones) TL 27 3001 (1986); 28 4825 (1987); 31 5157 (esters and lactones) (1990) Pure Appl Chem 58 1257 (1986) (esters and lactones) JACS 112 9263 (1990) SL 729 (1994) JOC 60 7879 (1995)
	various chiral amino alcohols (enantioselective)	

See also page 1717, Section 1; and page 1724, Section 2, for reactions with strong bases followed by protonation.

2.3. Cation Radical



JACS 110 2324 (1988)

2.4. Base-Promoted

Review: Syn 97 (1969)

 $\text{KNH}_2, \text{NH}_3$

JCS 1642 (1947)

Acct Chem Res 1 231 (1968)

Syn 97 (1969)

 $\text{KNH}(\text{CH}_2)_3\text{NH}_2, \text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$

Syn 754 (1978)

Org Syn 65 224 (1987)

Org Syn Coll Vol 8 553 (1993)

 LiNEt_4

JOC 23 1136 (1958)

JACS 86 5281 (1964)

 $\text{KO}-t\text{-Bu}, \text{DMSO}$

JACS 83 3731 (1961); 84 3164 (1962); 85 1553 (1963)

JCS 4234 (1963)

Ber 99 1737 (1966)

JOC 33 221 (1968); 58 2628 (1993)

JOC USSR 18 71 (1982)

cat $\text{KO}-t\text{-Bu}, \text{DMF}$

TL 31 43 (1990)



JOC 45 900 (1980)

 NaCH_2Ph

TL 467 (1964)

Na, alumina

JACS 87 4107 (1965)

JCS C 2149 (1967)

Angew Int 24 320 (1985)

K, alumina

Angew Int 24 320 (1985)

 MgO

CL 133 (1979)



TL 1191 (1964); 28 5887 (1987)

JCS C 82 (1966); 1903 (1968)

JCS Perkin I 1535 (1972); 1858 (1973)

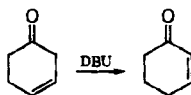
JOC 53 1860 (1988)

JACS 111 6666 (1989)

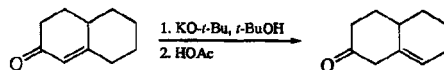


JOC 30 3235 (1965)

See also page 225, Section 2.9.

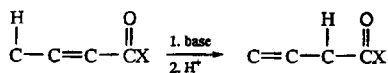


JOC 60 465 (1995)



TL 669 (1962)

JOC 30 2513 (1965)

 \underline{X}

OH

See page 1717, Section 1.

OR

See page 1724, Section 2.

 NR_2

See page 1778, Section 4.

2.5. Acid-Catalyzed

Review: Syn 405 (1970)

acid alumina

JACS 87 4107 (1965)

 $(\text{CO}_2\text{H})_2$, EtOH

JACS 75 5421 (1953)

HCl

JOC 57 4590 (1992)

HCl, BCl_3

TL 32 1635 (1991)

p-TsOH

JOC 59 5633 (1994)

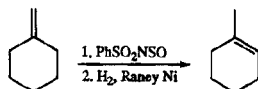
2.6. Sulfur Dioxide

JACS 99 5219 (1977); 113 3085 (1991)

JOC 48 4918 (1983)

TL 30 4621 (1989)

2.7. Ene Reaction-Reduction



TL 28 5017 (1987)

2.8. Iodine

JCS 2760 (1957)

JCS C 260 (1966) (plus $h\nu$)

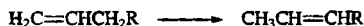
JOC 52 2586 (1987); 55 4807 (1990)

TL 29 2147 (1988); 36 8723 (1995)

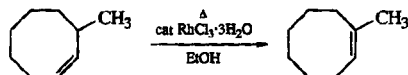
2.9. Transition Metal-Catalyzed

See also page 547, Section 3.

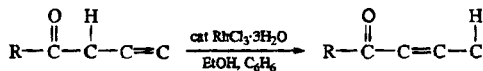
Review: C. W. Bird, "Transition Metal Intermediates in Organic Synthesis," Academic Press, New York (1967), Chpt 3



chiral Cp_2TiCl_2 , LiAlH_4 (enantioselective)	JACS 114 2276 (1992)
$\text{RuCl}_2(\text{PPh}_3)_3$	JOC 36 2497 (1971)
cat $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ -Dowex®1	TL 35 781 (1994)
cat $\text{ClRh}(\text{PPh}_3)_3$	JOC 59 952, 6142 (1994)
$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	JOC 36 2497 (1971)
$[(o\text{-CH}_3\text{C}_6\text{H}_4\text{O})_3\text{P}]_2\text{Ni}(\text{C}_2\text{H}_4)$, HCl	JOC 41 3020 (1976)
$\text{PdCl}_2(\text{PhCN})_2$	JACS 99 1673 (1977); 110 470 (1988); 112 8985 (1990) TL 28 5473 (1987)
Pd-C (H_2 activated)	JOC 56 3358 (1991)
$\text{PtCl}_2(\text{PPh}_3)_2$, SnCl_2	JOC 36 2497 (1971)



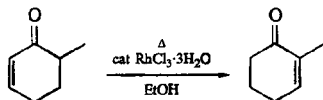
JACS 86 1776, 2516 (diene) (1964); 107 7352 (1985)
 Helv 50 2445 (1967) (diene)
 JOC 52 2875 (1987); 60 4559 (1995)
 TL 35 1503 (1994)



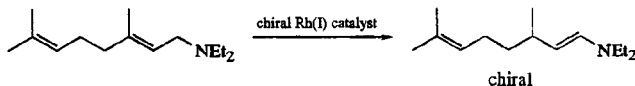
JOC 55 1096 (1990)
 JACS 112 8197 (1990)



<u>X</u>	<u>Catalyst</u>	
CH_2	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	JCS Perkin I 359 (1977) JOC 45 3017 (1980) Syn 952 (1983) Syn Commun 7 185 (1977)
	$\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	
CH_2CH_2	$\text{ClRh}(\text{PPh}_3)_3$ $\text{IrCl}(\text{CO})(\text{PPh}_3)_2$	TL 1263 (1974) TL 1263 (1974)
O	$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	JOC 52 1429 (1987) TL 31 5741 (1990)

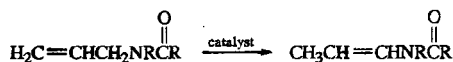


JACS 98 7102 (1976); 109 3025 (1987); 112 9284 (1990)
 TL 28 31 (1987)



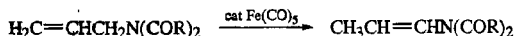
JACS 106 5208 (1984); 112 4897 (1990)
 Pure Appl Chem 57 1845 (1985)
 Syn 665 (1992) (review)
 Org Syn Coll Vol 8 183 (1993)

"Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 2



Catalyst

Fe(CO) ₅ , hv	JCS Perkin II 1954 (1973)
Fe ₂ (CO) ₉	JOC 57 5542 (1992)
HRuCl(PPh ₃) ₃	JOC 45 2139 (1980)
HRh(PPh ₃) ₄	JOC 45 2139 (1980)
HRh(CO)(PPh ₃) ₃	JOC 45 2139 (1980)
ClRh(PPh ₃) ₃	TL 2591 (1977); 31 2105 (1990)
Rh(ClO ₄)(BINAP)	Pure Appl Chem 57 1845 (1985)
RhCl ₃ ·3H ₂ O	TL 2591 (1977)

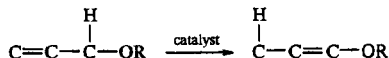


Ann Chim (Rome) 59 268, 762 (1969)
 JOC 45 2139 (1980)



Catalyst

Fe(CO) ₅	JOC 45 2139 (1980)
Pd(OAc) ₂ , cat dppe, <i>i</i> -Pr ₂ NEt, CF ₃ CO ₂ H	TL 36 4505 (1995)

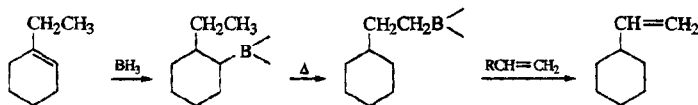


Catalyst

Fe(CO) ₅	JCS Perkin II 366 (1972)
H ₂ Ru(PPh ₃) ₄	TL 1415 (1979); 21 4927 (1980); 23 1079 (1982); 28 239 (1987)

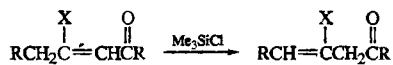
Catalyst	$\text{C}=\text{C}-\overset{\text{H}}{\underset{ }{\text{C}}}-\text{OR} \xrightarrow{\text{catalyst}} \overset{\text{H}}{\underset{ }{\text{C}}}-\text{C}=\text{C}-\text{OR} \quad (\text{continued})$
	CL 1435 (1981) JACS 109 5280 (1987); 111 6666 (1989) JOC 52 5700 (1987)
HRuCl(PPh ₃) ₃	TL 36 1887 (1995)
RuCl ₂ (PPh ₃) ₃ , NaBH ₄	JOC 53 1860 (1988)
Ru ₂ Cl ₄ (diop) ₃ -H ₂ (enantioselective)	SL 517 (1994)
H ₂ Ru(CO)(PPh ₃) ₃	TL 21 4927 (1980)
HRuCl(CO)(PPh ₃) ₃	TL 21 4927 (1980)
[(Ph ₃ P) ₂ RhCl] ₂	TL 32 23 (1991)
ClRh(PPh ₃) ₃	JOC 38 3224 (1973) CC 277 (1974) JACS 109 5446 (1987); 113 4037 (1991); 114 9419 (1992)
ClRh(PPh ₃) ₃ , DABCO	SL 514 (1990) TL 35 3593 (1994) JOC 60 3205 (1995)
Rh(ClO ₄) ₄ (BINAP)	Pure Appl Chem 57 1845 (1985)
[IrH ₂ (THF) ₂ (Ph ₂ PMe) ₂][PF ₆]	TL 36 1887 (1995)
[Ir(COD)(Ph ₂ PMe) ₂][PF ₆], H ₂	CC 694 (1978) Syn 305 (1981) TL 29 2413 (1988) JOC 53 4522 (1988); 55 4904 (1990)
NiCl ₂ (dppe), <i>i</i> -PrMgBr, Me ₃ SiCl	TL 36 1133 (1995)
PdCl ₂ (PhCN) ₂	JCS Perkin I 2870 (1973)
Pd(OH) ₂ , H ₂	JACS 111 6666 (1989)

2.10. Organoboranes



JACS 82 2074 (1960); 89 561, 567 (1967)

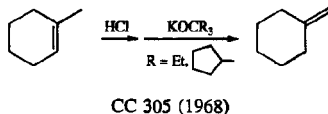
2.11. Trimethylsilyl Chloride



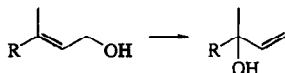
X = Ph, Br, I


TL 35 9585 (1994)

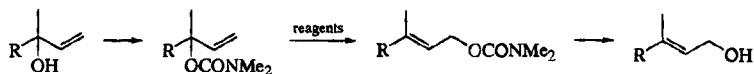
2.12. Addition–Elimination



3. Functional Group Rearrangement



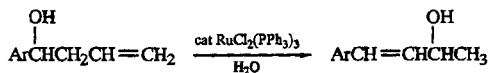
H ₂ SO ₄	JOC 59 5794 (1994)
NaH, CS ₂ , MeI/ <i>n</i> -Bu ₃ SnH/ <i>m</i> -ClC ₆ H ₄ CO ₂ H/HCl	Syn 1011 (1980)
<i>t</i> -BuO ₂ H, cat Ti(O- <i>i</i> -Pr) ₄ , diisopropyl tartrate/MsCl/Li, NH ₃	JOC 49 1707 (1984)
<i>t</i> -BuO ₂ H, cat Ti(O- <i>i</i> -Pr) ₄ , cat diisopropyl tartrate/MsCl or TsCl/Te, NaBH ₄	TL 31 5603 (1990) JOC 59 4311, 4760 (1994)
<i>t</i> -BuO ₂ H, cat Ti(O- <i>i</i> -Pr) ₄ , cat dialkyl tartrate/MsCl or TsCl/Te-HOCH ₂ SO ₂ Na·2H ₂ O-NaOH	JOC 58 718 (1993); 59 4760 (1994) TL 35 5583 (1994)
<i>t</i> -BuO ₂ H, cat Ti(O- <i>i</i> -Pr) ₄ , cat dialkyl tartrate/TsCl/Te, LiHBEt ₃	JOC 58 718 (1993)
<i>t</i> -BuO ₂ H, cat Ti(O- <i>i</i> -Pr) ₄ , cat diethyl tartrate, molecular sieves/MsCl or TsCl/NaI	TL 32 3961 (1991) JOC 59 1444 (1994)
<i>t</i> -BuO ₂ H, cat Ti(O- <i>i</i> -Pr) ₄ , cat diethyl tartrate/NaH, CS ₂ /K ₂ CO ₃ / <i>n</i> -Bu ₃ SnH, cat Et ₃ B	TL 35 6697 (1994)
<i>t</i> -BuO ₂ H, cat VO(acac) ₂ /MsCl/Li, NH ₃	JACS 109 3025 (1987)
<i>t</i> -BuO ₂ H, cat VO(acac) ₂ /MsCl/Na, NH ₃	TL 2621 (1976); 29 4913 (1988) CL 465 (1977) BCSJ 52 1757 (1979) JOC 55 227 (1990)
<i>t</i> -BuO ₂ H, cat VO(acac) ₂ /MsCl/Na naphthalene	TL 27 6353 (1986)
<i>t</i> -BuO ₂ H, cat VO(acac) ₂ /() ₂ CS/ <i>n</i> -Bu ₃ SnH	JCS Perkin I 2363 (1981) TL 29 4909 (1988)
PhCMe ₂ O ₂ H, cat VO(acac) ₂ , 2,6-lutidine/CBr ₄ , PPh ₃ /Zn, HOAc, THF	JACS 109 6187 (1987)
<i>o</i> - or <i>p</i> -NO ₂ C ₆ H ₄ SeCN, <i>n</i> -Bu ₃ P/H ₂ O ₂	CC 770 (1978) JOC 50 2981 (1985)
MsCl, Et ₃ N/(PhSe) ₂ , NaBH ₄ /H ₂ O ₂	JOC 60 615 (1995)

Hg(O₂CCF₃)₂ / PPh₃

JACS 100 4822 (1978)

PdCl₂(CH₃CN)₂

Can J Chem 62 791 (1984)



JACS 117 12869 (1995)



HOAc

JCS 396 (1946)

HCl

JCS 396 (1946)

HNO₃

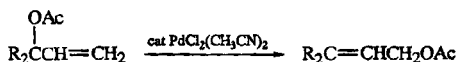
JOC 36 3951 (1971); 59 5093 (1994)

H₃PO₄

JOC 58 328 (1993)



See page 1201, Section 1.



JACS 94 5200 (1972); 102 7587 (1980); 111 3456 (1989)

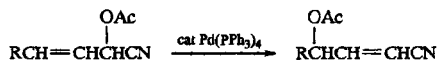
TL 321 (1979); 28 4131, 5655 (1987); 29 1017, 1157 (1988); 33 7039 (1992); 34 5923 (1993)

JOC 46 5005 (1981); 55 4614 (1990); 58 7490 (1993); 59 3347 (1994)

Tetr 40 1791 (1984)

Can J Chem 62 791 (1984) (carbonates also)

SL 491 (1994)



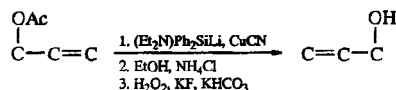
Syn 687 (1982)

BF₃·OEt₂

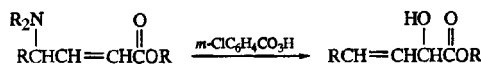
JOC 55 5564 (1990)

Ph₂BBr

JACS 110 4085 (1988)



JACS 114 3989 (1992)



TL 32 4481 (1991)

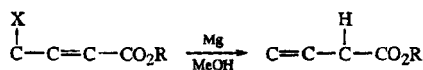
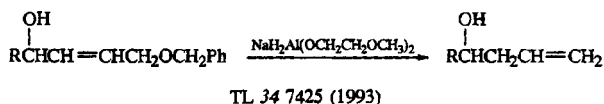
4. Reductive Transposition



<u>X</u>	<u>Reagent(s)</u>	
Cl	(NH ₄)O ₂ CH, cat Pd ₂ (DBA) ₃ ·CHCl ₃ , cat <i>n</i> -Bu ₃ P Ph ₂ SiH ₂ , cat Pd(PPh ₃) ₄	CL 1017 (1984) Israel J Chem 24 82 (1984)
Cl, I	SmI ₂ , H ₂ O	TL 34 6931 (1993)
O ₃ SR	NaO ₂ CH, cat Pd(DBA) ₂ , cat P(C ₆ H ₄ OMe- <i>o</i>) ₃ , 15-crown-5	TL 33 3307 (1992)
OPh	(NH ₄)O ₂ CH, cat Pd ₂ (DBA) ₃ ·CHCl ₃ - <i>n</i> -Bu ₃ P (NH ₄)O ₂ CH, cat PdCl ₂ (PPh ₃) ₂	CL 1017 (1984) TL 613 (1979)
OH	Na, NH ₃ , EtOH NaH, CS ₂ /MeI/ <i>n</i> -Bu ₃ SnH LiAlH ₄ ClPO(O- <i>i</i> -Pr) ₂ , py/ NaFe(CO) ₂ Cp / HBF ₄ / NaI <i>p</i> -TsNHNH ₂ / NaOAc, HOAc	JOC 59 5419 (1994) TL 21 1767 (1980) JOC 57 2523 (1992) JACS 112 8126 (1990) JOC 51 2126 (1986) JACS 112 6429 (1990)
O ₂ CH	cat Pd(acac) ₂ - <i>n</i> -Bu ₃ P cat Pd(OAc) ₂ - <i>n</i> -Bu ₃ P	JOC 57 1326 (1992) SL 113 (1993) JOC 57 1326 (1992) SL 291 (1993)
O ₂ CR	(NH ₄)O ₂ CH, cat PdCl ₂ (PPh ₃) ₂ (NH ₄)O ₂ CH, cat Pd ₂ (DBA) ₃ ·CHCl ₃ - <i>n</i> -Bu ₃ P NaO ₂ CH, cat Pd(OAc) ₂ , cat PPh ₃ , cat 15-crown-5 Me ₃ Si(OSiHMe) ₄₀ OSiMe ₃ , cat Pd(PPh ₃) ₄ <i>n</i> -BuZnCl, cat Pd(OAc) ₂ , cat PPh ₃	TL 613 (1979) CL 1017 (1984) SL 949 (1994) Israel J Chem 24 82 (1984) SL 949 (1994)

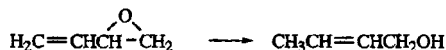


X	Reagent(s)	
OCO ₂ Me	(NH ₄)O ₂ CH, cat Pd(OAc) ₂ - n-Bu ₃ P	CL 1017 (1984)
	(NH ₄)O ₂ CH, cat Pd ₂ (DBA) ₃ ·CHCl ₃ -n-Bu ₃ P	CL 1017 (1984)
	HCO ₂ H, 1,8-bis- (dimethylamino)naphthalene, cat Pd ₂ (DBA) ₃ ·CHCl ₃ , cat chiral ligand (enantioselective)	JACS 116 775 (1994)
SO ₂ Ph	LiAlH ₄ , CuCl ₂	JACS 107 1034 (1985)
	HCO ₂ H, Et ₃ N, cat Pd(acac) ₂ - n-Bu ₃ P	SL 113 (1993)
NO ₂	HCO ₂ H, Et ₃ N, cat Pd(acac) ₂ - n-Bu ₃ P	SL 113 (1993)
	NaBH ₄ , NaBH ₃ CN, n-BuZnCl or LiHB(sec-Bu) ₃ ; cat Pd(PPh ₃) ₄ ; cat phosphine	JOC 51 3734 (1986)
⁺ PPh ₃	LiAlH ₄	JOC 49 4084 (1984)
SiMe ₃	CF ₃ CO ₂ H	TL 30 5777 (1989)



X = Cl, Br, OR, O₂CR, epoxide, aziridine

JOC 58 1523 (1993)



BH ₃	Rocz 47 771 (1973); 48 467 (1974) Syn 62 (1979)
NaBH ₃ CN, BF ₃ ·OEt ₂	JOC 46 5214 (1981)
LiHBEt ₃	TL 3775 (1976)
i-Bu ₂ AlH	JACS 95 957 (1973)
LiAlH ₄	TL 3775 (1976)
LiAlH ₄ , CuCN	SL 759 (1993)
Li/NH ₃	JACS 95 957 (1973)

Ca, NH₃

JACS 95 957 (1973)

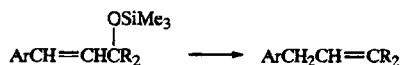
TL 28 2021 (1987)

Cp₂TiCl

TL 33 7973 (1992)

SmI₂, ROH

JOC 51 5259 (1986)

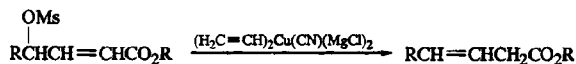
Li, sonication/NH₄Cl

JOC 59 5093 (1994)

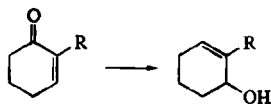
Li, NH₃/NH₄Cl

TL 31 1339 (1990)

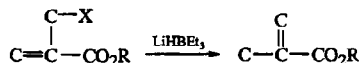
JOC 58 328 (1993)



TL 32 4969 (1991)



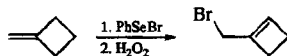
See page 303, Section 54.3.



X = Br, OAc

Angew Int 22 796 (1983)

5. Oxidative Transposition



TL 33 7141 (1992)

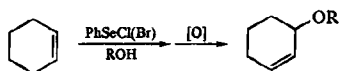
See also page 614, Section 2.

(PhSe)₂, MgSO₄, MeOH, electrolysis

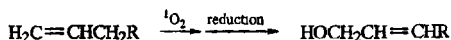
JACS 103 4606 (1981)

PhSeCl, MeOH/*m*-ClC₆H₄CO₂H

TL 27 6361 (1986)



JOC 39 429 (1974)



Angew 69 579 (1957)

A. Schonberg, "Preparative Organische Photochemie," Springer Verlag, Berlin (1958), p 47

JACS 90 975 (1968); 101 275 (1979); 112 5193, 6417 (1990); 113 3180 (1991); 114 6549 (1992); 115 3008, 5041, 7226 (1993); 117 2694, 3976 (1995)

Adv Photochem 6 1 (1968)

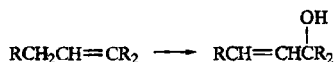
Acct Chem Res 1 104 (1968); 13 419 (1980) (mechanism)

Helv 61 2777 (1978)

Tetr 37 1825 (1981)

JOC 53 3124 (1988); 56 5778 (1991); 58 7204 (1993); 59 3335 (1994)

TL 30 4875 (1989); 33 3461 (1992); 34 8423 (1993); 35 1681 (1994); 36 4291 (1995)



"PhSeOH" / *t*-BuO₂H

TL 3967 (1978)

JOC 43 1688 (1978)

(PhSe)₂, MgSO₄, H₂O, CH₃CN, electrolysis

JACS 103 4606 (1981)

PhSeCl, H₂O / *m*-ClC₆H₄CO₂H

TL 27 2391 (1986)

PhSeBr, AgO₂CCF₃ / H₂O, MeOH, NaHCO₃ / H₂O₂

JACS 106 1446 (1984)

epoxidize / PhSeNa / [O]

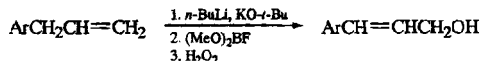
JACS 95 2697 (1973); 106 7854 (1984); 107 1691, 1777 (1985); 111 3374 (1989)

Tetr 34 1049 (1978)

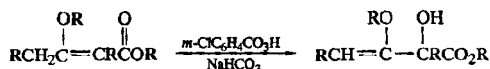
JOC 51 2148 (1986); 52 2644 (1987); 59 720, 1444 (1994)

epoxidize / *i*-Bu₂AlSePh / *m*-ClC₆H₄CO₂H / Et₃N, Δ

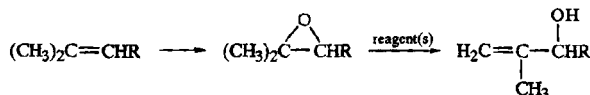
JOC 50 5897 (1985)



TL 32 2475 (1991)



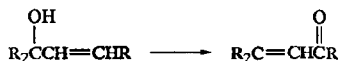
TL 35 3103 (1994)



See page 272, Section 19.



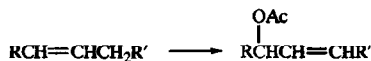
O_2 , NaOH, $P(OEt)_3$, chiral catalyst	TL 29 2835 (1988)
$NaO-t-Bu/O_2$	JOC 33 3695 (1968)
$KN(SiMe_3)_2$ / camphorsulfonyl oxaziridine	JACS 114 9419 (1992)
Me_3SiI , $(Me_3Si)_2NH$ / $m-ClC_6H_4CO_2H$ / $n-Bu_4NF$	JACS 110 5568 (1988); 111 6287 (1989); 115 6078 (1993)



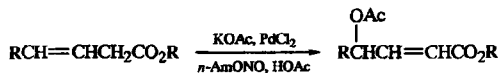
See page 1249, Section 19.



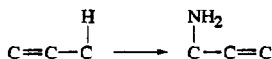
O_2 , hv, porphine ($R = H$, alkyl)	JOC 48 4135 (1983) TL 34 4435 (1993)
Ag_2CrO_4 , I_2 , py ($R = alkyl$)	JOC 56 1936 (1991)
SeO_2 , HOAc / CrO_3/Zn , HOAc ($R = alkyl$)	JOC 57 3347 (1992)



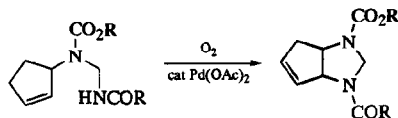
PhSeBr, HOAc / H_2O_2	JACS 106 1446 (1984) JOC 56 5285 (1991)
SeO_2 , HOAc	JOC 57 3347 (1992)



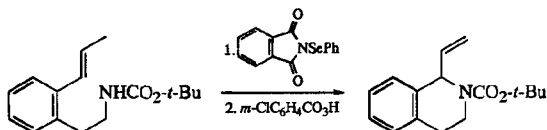
TL 22 131 (1981)



See page 761, Section 3.



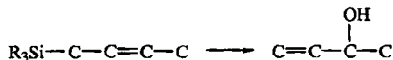
TL 35 9281 (1994)



JACS 107 1421 (1985)

6. Metal and Heteroatom Displacement

See also page 689, Section 1.



$\text{CH}_3\text{CO}_3\text{H}$, buffer

CC 679 (1976)

$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}/\text{H}^+$

CC 79 (1977)

TL 23 1267 (1982)

JOC 49 4224 (1984)

$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}/n\text{-Bu}_4\text{NF}^-$

TL 24 4153 (1983); 32 1583 (1991)

JOC 55 1106 (1990)

$\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_3/\text{HOAc}$

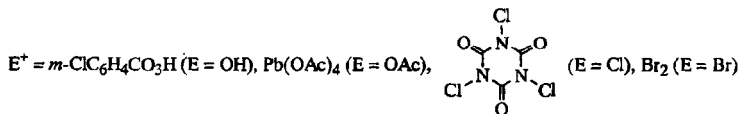
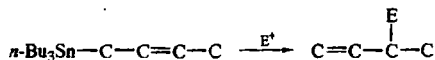
TL 31 7567 (1990); 34 5421 (1993)

cat OsO_4 , $\text{Me}_3\text{NO}\cdot 3\text{H}_2\text{O}/\text{KH}$

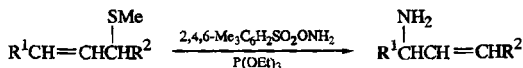
JOC 55 1106 (1990)

$[\text{PhSeSe}(\text{Me})\text{Ph}]\text{BF}_4^-/\text{NaIO}_4$

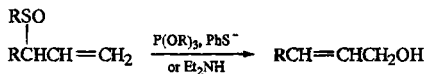
JACS 112 4357 (1990)



JACS 115 5934 (1993)



TL 32 5029 (1991)

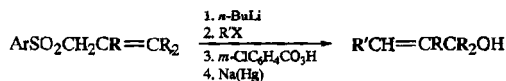


TL 28 1925, 5865 (1987)

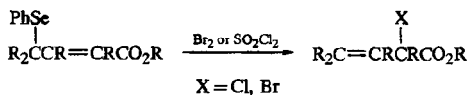
JOC 52 4634 (1987); 54 2779 (1989); 57 441, 3078, 5060 (1992)

JACS 112 4357 (1990)

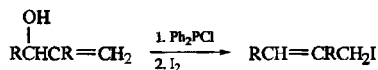
See also page 351, Section 1.



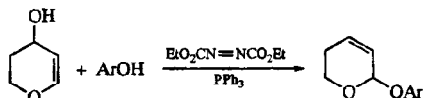
TL 441 (1979)



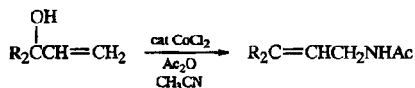
TL 34 7417 (1993)



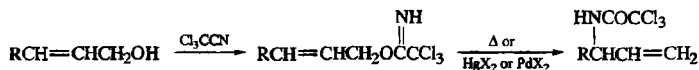
TL 34 2993 (1993)



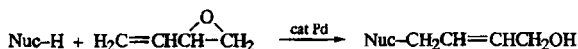
TL 35 3661 (1994)



TL 32 6965 (1991)



See page 1857, Section 15.

Nuc-H $\text{R}_3\text{SiOAr}, \text{R}_3\text{SiO}_2\text{CR}$

JOC 53 189 (1988)

 Ph_3SiOH

TL 34 1421 (1993)

 ArOH

TL 26 5615 (1985)

 RCO_2H

TL 26 5615 (1985)

Org Syn Coll Vol 8 13 (1993)

 NaN_3

TL 29 4851 (1988)

 R_2NH

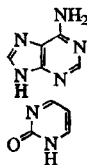
TL 22 2575 (1981)

JACS 111 4988 (1989)

JOC 56 4990 (1991)

JACS 110 621 (1988)

JOC 57 5861 (1992)

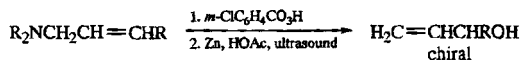


JACS 110 621 (1988)

 $\text{TsNH}_2, \text{NaNHTs}$

JOC 60 6091 (1995)

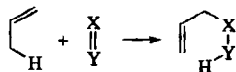
For carbon nucleophiles, see page 236, Section 8.



SL 969 (1994)

7. Ene Reaction

See further examples in the following Section 8.



Angew Int 8 556 (1969); 17 476 (1978) (intramolecular); 23 876 (1984)

Acct Chem Res 13 426 (1980) (review)

Tetr 37 3927 (1981)

D. F. Taber, "Intramolecular Diels-Alder and Alder Ene Reactions," Springer Verlag, New York (1984) (review)

W. Carruthers, "Cycloaddition Reactions in Organic Synthesis," Pergamon Press, Oxford (1990), Chpt 5 (review)

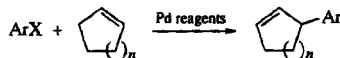
Chem Rev 92 1021 (1992) (review)

TL 35 6903, 6907 (1994) (both intramolecular)

Syn 347 (1995) (imino ene reactions)

8. Alkylative Transposition

See also page 1063, Section 5; page 1302, Section 9.2; page 1384, Section 2.2; page 1400, Section 2.7; page 1528, Section 22 (Carroll Reaction); page 1851, Section 12; page 1855, Section 13; page 1858, Section 16; and page 1859, Section 17.

XPd reagents

Br or I

Pd catalyst


JOC 43 2952, 4110 (1978); 44 21 (1979); 52 4130 (1987) (intramolecular); 53 5588 (1988) (intramolecular); 55 407, 2464 (1990); 56 3711 (1991); 57 2093, 4015, 4571 (chiral, intramolecular), 4690 (1992); 58 2557 (1993); 60 2016, 4322 (both intramolecular), 5356 (1995)

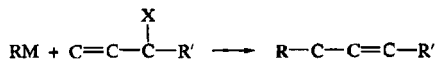
Tetr 35 329 (1979)

TL 29 905, 2915 (intramolecular), 2919 (intramolecular), 3785 (intramolecular) (1988); 30 2603 (1989); 30 3075 (1990) (intramolecular); 32 687 (1991) (intramolecular); 33 4859 (intramolecular), 6845

		(enantioselective) (1992); 34 5205 (intramolecular), 5265 (1993); 35 2573 (1994) (intramolecular) IACS 112 6959 (1990) (intramolecular); 115 11028 (1993) (intramolecular) SL 715 (1992); 393 (1993); 499 (1994) Pure Appl Chem 64 421 (1992) (enantioselective); 66 1423 (1994) (intramolecular, review)
OTf	Pd catalyst	JACS 113 1417 (1991) Pure Appl Chem 64 421 (1992) JOMC 428 267 (1992) TL 33 1485 (1992); 35 1227 (1994)
N ₂ ⁺	cat PdCl ₂ -NaO ₂ CH or Pd(DBA) ₂	Tetr 37 31 (1981)
NH ₂	<i>t</i> -BuONO, cat Pd(DBA) ₂ <i>t</i> -BuONO, Pd(OAc) ₂	CL 551 (1980) JOC 46 4885 (1981) JOC 45 2359 (1980)
SnR ₃	Pd(OAc) ₂	JOC 54 29 (1989)
HgX (X = OAc, Cl)	Pd(II) salts	JACS 93 6896 (1971); 100 287 (1978) Organomet Chem Syn 1 455 (1972) JOC 43 4110 (1978); 48 399, 2870 (1983); 54 29 (1989); 56 3711 (1991)



CH ₃ Li / CuI / RLi / [<i>n</i> -Bu ₃ PNMePh]I	JACS 99 2361 (1977); 100 4610 (1978) JOC 46 2144 (1981) TL 23 557 (1982); 27 6353 (1986)
CH ₃ MgBr, cat NiCl ₂ L ₂ (R = CH ₃)	CC 681 (1981)
Me ₂ C=CCIN  / cat CuI, HMPA / RMgX	TL 24 5745 (1983)

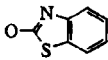
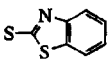
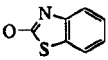


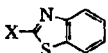
See also page 386, Section 21.

Reviews:


- Tetr 36 1901 (1980)
 Org Rxs 41 135 (1992) (organocopper reagents)
 SL 769 (1992) (organocopper reagents)

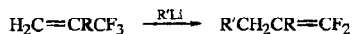
RM	X	
<i>n</i> -Bu ₃ SnCHRI, Zn-Cu/CuCN	Cl, Br	SL 891 (1992)
RLi, cat CuI	SO ₂ Ph	TL 29 781 (1988)
MeLi/RCu	O ₂ CNHR (chiral)	JOC 55 1984 (1990)
Me ₂ NN=CRCHRLi, cat CuI	O ₂ CR	CL 1521 (1982) (4-alken-3-olide)
EtMgBr, cat Cp ₂ ZrCl ₂	OR	JACS 115 8485 (1993)
PhMgBr, Ni catalyst	Cl, OR, OSiR ₃ , OH	CC 313 (1981)
RMgX, cat Ni(dppe) (?) (R = 1°, 2° alkyl)	OTHP	TL 29 3373 (1988)
PhMgBr, cat PdCl ₂ L ₂	OSiEt ₃	CC 313 (1981)
RMgX, cat CuCl	O ₂ CR	TL 633 (1979) (enynne synthesis) JOC 51 2884, 2892 (1986)
RMgX, cat CuBr	OR	TL 3831 (1975); 31 6385 (1990) HSCF II 309 (1979) Tetr 35 1517 (1979) (S _N 2 or S _N 2')
RMgX, cat CuBr·SMe ₂	O ₂ CR	JOC 51 1612 (1986)
RMgX, cat CuI	O ₂ CR	TL 23 3583 (5-alken-4-olide, 6-alken-5-olide), 3587 (6-alken-5-olide) (1982); 34 91 (1993) [4-(1-alkenyl-1,3-dioxolan-2-one)] CL 1521 (1982) (4-alken-3-olide)
RMgX, cat CuCN	O ₂ CR	JOC 51 2884, 2892 (1986); 54 2369, 3374 (1989) JACS 110 7128 (1988); 112 6615 (1990) TL 29 3201 (1988) TL 32 855 (1991) JOC 57 5692 (1992); 59 332 (1994)
	OMs	JACS 110 5216 (1988); 112 6615 (1990)
	SO ₂ Ph	JACS 110 5216 (1988); 112 6615 (1990)
RMgX, cat CuCN·2LiCl	OPO(OR) ₂	SL 689 (1993)
RMgX, cat chiral CuSar	OAc, OPO(OR) ₂	TL 35 5931 (1994); 36 3059 (1996)
RMgX, cat CuCl·2LiCl	Cl	JOC 59 4126 (1994)
ArMgX, CuCl·2LiCl	Cl, Br, I	JOC 59 4126 (1994)
RMgX, cat Li ₂ CuCl ₄	Cl	TL 23 3115 (1982) JACS 112 6615 (1990)

	Br	Helv 65 684 (1982) TL 23 3115 (1982)
	OAc	CC 827 (1987) JACS 112 6615 (1990) JACS 112 6615 (1990)
RMgX, cat Cu(acac) ₂	SO ₂ Ph	TL 2393 (1979) Tetr 39 3283, 3289 (1983)
RMgX(Li), CuBr·SMe ₂	SO ₂ Ph	JOC 51 1612 (1986) (5-alken-4-olide)
RMgX, CuX (X = Br, I)	O ₂ CR	Syn 885 (1979) JOMC 231 179 (1982) JOC 46 4482 (1982); 47 4482 (1982)
		CC 1085 (1978); 1252 (1986) (S _N 2 or S _N 2')
		JCS Perkin I 2953 (1983)
RMgX (X = Cl, Br), CuBr, LiBr	OAc	Syn 469 (1982)
RMgX, CuCN, LiCl	OAc	TL 34 7565 (1993)
R ₃ Al, cat CuCN	OPO(OEt) ₂	SL 183 (1995)
RTi(OR') ₃ , RTi(OR') ₄ Li or R ₂ Ti(OR') ₃ Li; cat CuI·2LiCl	Cl, Br, OPO(OEt) ₂	JOC 56 5489 (1991); 58 5121 (1993)
RCH ₂ CH ₂ ZrClCp ₂ , cat CuCN	Cl, Br, OPO(OEt) ₂	TL 33 5857 (1992)
RCu	Br	JOC 49 1838 (1984)
	O ₂ CR	JOC 51 1612 (1986) (5-alken-4-olide) TL 31 1869 (1990)
RC≡CCu		TL 3873 (1979)
RCu·BF ₃	Cl, Br	JACS 99 8068 (1977); 102 2318 (1980) JOC 49 1838 (1984); 58 5121 (1993)
	OH	JOMC 156 C9 (1978) JACS 102 2318 (1980)
	O ₂ CR	JOC 51 1612 (1986) (5-alken-4-olide)
	SO(NMe)Ph	JACS 113 1442 (1991) (enantioselective)
RCu, LiI, BF ₃ ·SMe ₂	SO(NMe)Ph	JACS 117 2453 (1995)
RCu·2 <i>n</i> -Bu ₃ P	OR	TL 22 1809 (1981)
R ₂ CuLi	Cl	JACS 92 737 (1970); 112 6615 (1990) JOC 57 2753 (1992)
	Br	JOC 52 3394 (1987)

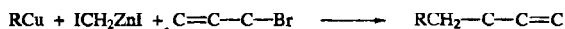
RM	X	
	O ₂ CR	CC 43 (1969) IACS 92 735 (1970); 94 5379 (1972); 95 6832 (1973); 98 7854 (1976); 101 1035, 2493 (1979); 109 8117 (1987) TL 4439 (1976); 1035 (1977); 23 3093 (1982) JOMC 136 103 (1977) Tetr 35 1517 (1979) JCS Perkin I 2093 (1980); 1729 (1981) (both 5-alken-4-olides) JOC 46 2591, 5304 (1981); 48 1531, 3986 (1983); 50 5495 (1985) (relative rates); 51 1612 (1986) (5-alken-4-olide); 52 5452 (1987); 54 3882 (1989); 58 817 (1993) Syn 469 (1982) CL 1521 (1982) (4-alken-3-olide) TL 22 119 (1981) JOC 45 4026 (1980) JACS 101 1035 (1979); 110 7128 (1988) TL 23 3093 (1982) JOC 48 715, 1404 (1983) JOC 56 1349 (1991) TL 32 855 (1991) JACS 108 7420 (1986) CC 434 (1980) CC 434 (1980) JACS 109 6396 (1987) TL 29 781 (1988)
	OCH ₂ OCH ₃	
	OAr	
	OCNHPh	
	OMs	
	OTs	
	SOPh	
	SO ₂ Ph	
R ₂ CuLi·BF ₃	OTs, OMs	JACS 108 7420 (1986)
R ₂ CuLi·2BF ₃	OTs	JACS 108 7420 (1986)
R ₂ CuLi, Me ₃ SiCl	OH	TL 28 5521 (1987)
R ₂ CuLi, ZnCl ₂	Cl	JOC 58 5121 (1993)
R ₂ CuMgX	O ₂ CR	TL 4439 (1976); 23 3583 (1982) (5-alken-4-olide) CL 1521 (1982) (4-alken-3- olide) Can J Chem 61 632 (1983) JOC 58 817 (1993); 59 5596 (1994) JOC 56 1349 (1991)
	OMs	
	 (X = O, S)	JOC 55 2294 (1990); 57 4546 (1992)

R_2CuZnX	Cl, Br	JACS 111 3091 (1989) (diastereoselective)
$RCu(CN)MgX$	Br, OAc OMs	TL 27 5095 (1986) JOC 56 1349 (1991)
$RCu(CN)MgX \cdot BF_3$	O_2CR OMs	TL 34 91 (1993) JOC 56 4370 (1991); 58 1207 (1993)
$RCu(CH_2SOCH_3)Li$	OAc	JOC 52 1885 (1987)
$[RCu(CN)CH_2SOCH_3]Li_2$	OAc	JOC 52 1885 (1987)
$RCu(X)Li$ ($X = CN, SPh$)	OAc	JOMC 136 103 (1977)
$RCu(CN)Li$	Br O_2CR	TL 27 5095 (1986) JOC 45 4256 (1980) (5-alken-4- olide); 48 1404, 3986 (1983); 49 422 (1984); 51 1612 (5- alken-4-olide), 4492 (1986)
	OMs	TL 27 5095 (1986) TL 32 855 (1991) JOC 56 1349 (1991)
$RCu(CN)Li \cdot BF_3$	OMs	CC 1596 (1987) JACS 111 4864 (1989) JOC 54 4055 (1989); 56 4370, 5834 (1991)
	O_2CR	TL 34 91 (1993)
$R_2Cu(CN)Li_2$	OMs Br	JACS 108 7420 (1986) TL 30 7399 (1989)
$R_2Cu(CN)Li_2 \cdot BF_3$	OTs, OMs	JACS 108 7420 (1986); 111 4864 (1989) CC 1596 (1987) JOC 54 4055 (1989)
$R_2Cu(CN)(ZnCl)_2$	OMs	TL 33 3783 (1992) JOC 57 1024 (1992)
$RCu(NCy_2)Li$	Cl	JACS 104 5824 (1982)
$RCu(PPh_2)Li$	Cl	JACS 104 5824 (1982)
$Li_2Cu_3Me_5$	OCONHPh	TL 23 3093 (1982); 24 4477 (1983) JOC 51 1264 (1986); 52 897 (1987)
$(R_3BMe)Li, CuBr$	Cl, Br	BCSJ 50 2199 (1977)
$R_2Zn, TMEDA$	Cl	CL 357 (1993) JOC 58 5121 (1993)
$R_2Zn \cdot 2LiCl, HMPA$ or TMEDA	Cl, Br, $OPO(OR)_2$	JOC 58 5121 (1993) CL 357 (1993)

RM	X	
RZnCl or R ₂ Zn, cat CuBr·SMe ₂	Cl	JACS 109 8056 (1987) TL 29 5155 (1988)
(RO ₂ CCH ₂ CH ₂) ₂ Zn, cat CuBr·SMe ₂	Cl, Br	See page 1724, Section 2.
ArCH ₂ Cu·ZnI ₂	Br	JOC 58 2694 (1993)
RCu(CN)ZnX	Cl, Br	JOC 56 1145, 5974 (1991); 57 5425 (1992); 58 2694 (1993) TL 36 1023 (1995)
NCCH ₂ CH ₂ Cu(CN)ZnI	Cl, Br	TL 29 2395 (1988)
(EtO) ₂ POCH ₂ CH ₂ Cu(CN)ZnI	Br	TL 31 1833 (1990)
AcOCH ₂ Cu(CN)ZnBr	Br	JOC 55 4791 (1991)
RCO ₂ CH ₂ Cu(CN)ZnI	Br	JOC 54 5202 (1989); 58 588 (1993)
 NCHRCu(CN)ZnX	Br	JOC 58 588 (1993)
PhCH ₂ O ₂ CCH(NHBoc)-CH ₂ Cu(CN)ZnI	Cl, Br, OTs	JOC 60 2210 (1995)
ArCu(CN)ZnX	Br, I	JOC 53 5789 (1988); 56 1445 (1991) TL 31 4413 (1990); 35 1047 (1994)
R ₂ Zn, CuCN·2LiCl	Br	JOC 52 1956 (1992); 60 3311 (1995) TL 34 5261 (1993)
RHgX, hv (R = 3° > 2° alkyl)	Cl, Br, I, SPh, SO ₂ Ph, <i>n</i> -Bu ₃ Sn, O ₃ SPh, OAc, OAr, OSiR ₃	JACS 111 4921 (1989)
RHgX, Li ₂ PdCl ₄ (R = aryl, vinyl)	Cl, OAc	JACS 90 5531 (1968); 100 287 (1978) JOC 43 2870 (1978); 46 1432 (1981); 54 4142 (1989) JOMC 156 45 (1978)

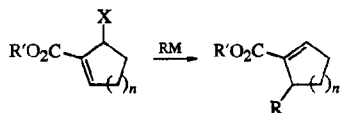


TL 36 5003 (1995)



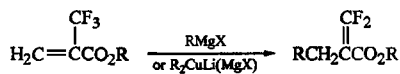
R = CN, CH₂CN, R₂N, Ar, RS

JACS 111 6474 (1989)

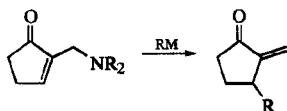


$n = 1, 2$; $X = \text{OAc}, \text{OSiMe}_3$; $\text{RM} = \text{RMgX-cat Cu(I)}, \text{RCHLiCO}_2\text{R}$

TL 28 5521 (1987)

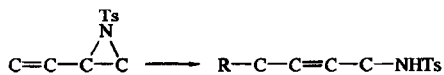


JOC 54 5630 (1989)



$\text{ThCu(CN)(CH=CHR)Li}_2$ JOC 53 5590 (1988)

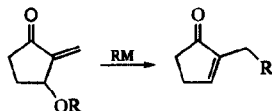
$\text{R}_2\text{CuLi(MgX)}, \text{ZnBr}_2$ JOC 55 408 (1990)



$\text{RCu} \cdot \text{BF}_3$ JOC 59 4875 (1994)

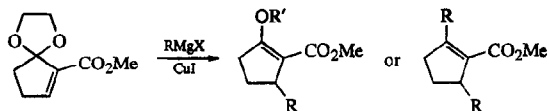
$\text{RCu(CN)Li} \cdot \text{BF}_3$ JOC 59 4875 (1994)

R_2CuLi JOC 59 4037 (1994)

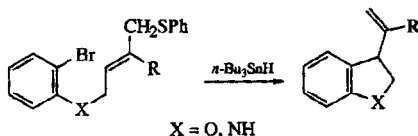


$\text{RM} = \text{R}_2\text{CuLi}, \text{RCu(CN)Li}$ or RCu(CN)MgX

JOC 53 5590 (1988)



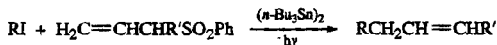
TL 34 4979 (1993)



TL 23 2575 (1982)

JACS 110 4796 (1988); 112 5230 (1990)

JOC 54 1238 (1989); 55 5823 (1990)



JOC 54 5845 (1989)



Review: Chem Rev 89 1503 (1989) (organocopper reagents)

RLi (R = alkyl, aryl)

TL 4419 (1975); 22 577 (1981); 29 4405 (1988)

 R_3B, O_2 (R = alkyl)

JACS 93 2792 (1971)

 $RCH=CHB \begin{array}{c} O \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \end{array}$, Ni or Pd catalyst

JOMC 233 C13 (1982)

RLi or RMgX, cat CuX (X = Cl, Br, I; R = alkyl, allyl, aryl, vinyl)

TL 2027 (1978); 2051 (1979)

Syn 528 (1978)

CL 185 (1980)

JOC 46 239 (1981); 50 1607 (1985)

Steroids 37 361 (1981)

JACS 105 3360 (1983)

RMgX, cat CuBr·SMe₂

JACS 117 7379 (1995)

RMgX, CuBr·SMe₂ (R = 1° alkyl, vinylic)

TL 29 4521 (1988)

RMgX, cat CuI

JOC 59 4037 (1994)

RMgX, CuI, SMe₂JACS 105 6515 (1983) (R = *i*-Pr₃SiC≡CCH₂); 106 723, 6006 (1984)

JOC 49 1707 (1984)

RMgX, CuCN

JOC 50 3988 (1985); 52 1106 (1987)

TL 30 2075 (1989)

R₂CuLi (R = alkyl, vinylic, aryl)

JACS 92 4978, 4979 (1970); 93 3046, 3047 (1971); 103 2114 (1981)

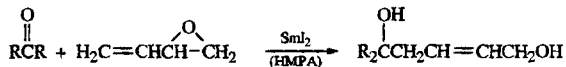
Syn 528 (1978)

TL 2027 (1978); 2051 (1979); 28 4985 (1987); 29 913, 4405 (1988); 31 3691 (1990)

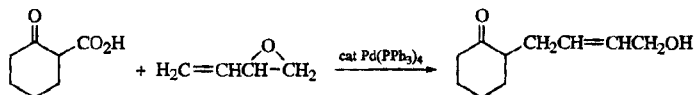
JOC 46 122 (1981); 53 4274 (1988); 56 2225 (1991); 57 115 (1992)

Steroids 37 361 (1981)

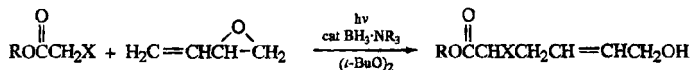
$R_2CuMgBr$	J Chem Res (S) 294 (1983) JOC 53 4274 (1988)
$(RCuC\equiv CR')Li$ (R = alkyl, vinylic; R' = <i>n</i> -Pr, <i>n</i> -Bu)	TL 675 (1979) JCS Perkin I 2084 (1980); 683 (1983)
$RCu(CH_2SOCH_3)Li$	JOC 52 1885 (1987)
$RCu(CN)Li$ (R = alkyl, aryl, vinylic)	JOC 44 4467 (1979); 46 4389, 5379 (1981); 52 4898 (1987); 53 4274 (1988); 55 1540 (1990); 56 2225 (1991); 57 115 (1992) TL 675 (1979); 33 5685 (1992); 36 35 (1995) Syn 872 (1980) JACS 103 2907 (1981); 104 3165 (1982)
$RCu(CN)Li, BF_3 \cdot OEt_2$	JOC 56 5496 (1991)
$R_2Cu(CN)Li_2$ (R = alkyl, aryl, vinylic)	JACS 104 2305 (1982) JOC 53 4274 (1988); 56 2225, 5496 (1991) TL 30 6817 (1989)
$R_2Cu(CN)Li_2$ (R = allylic)	JACS 112 4063 (1990)
$R_2Cu(CN)Li_2, BF_3 \cdot OEt_2$ (R = 2-furyl)	TL 29 3045 (1988)
$ThCu(CH=CHR)(CN)Li_2$	SL 761 (1993)
$RCu(CN)MgX$	JOC 50 3988 (1985); 54 26 (1989)
$(RO_2CCH_2CH_2)_2Zn$, cat CuBr·SMe ₂	JACS 109 8056 (1987)
$RSnR'_3$, cat $PdCl_2(CH_3CN)_2$ (R = aryl, vinylic)	JACS 110 4039 (1988); 115 2970 (1993)
$RHgCl$ (R = aryl, vinylic), Li_2PdCl_4	TL 27 2211 (1986)
RX (RX = ArI or vinylic iodide or triflate), cat $Pd(OAc)_2$, NaO_2CH , n -Bu ₄ NCl, i -Pr ₂ NEt	JOC 58 804 (1993)
$HCR'XY$ (X, Y = electron-withdrawing groups), Pd catalyst (R = CR'XY; X, Y = SR, COR; COR, COR; COR, CO ₂ R; SR, CO ₂ R; SO ₂ R, CO ₂ R; CO ₂ R, CO ₂ R; SR, CN; SO ₂ R, SO ₂ R; H, NO ₂)	TL 22 2575 (1981); 25 1921 (1984); 27 3881 (1986) (intramolecular); 30 6625 (1989); 32 2025, 2193 (1991); 33 717 (1992) (intramolecular) JACS 103 5969 (1981); 104 6112 (1982) (intramolecular); 105 147, 5940 (1983) (both intramolecular); 110 6265 (1988) (intramolecular); 113 1044 (1991) CC 985 (1983) (intramolecular) SL 763 (1994)



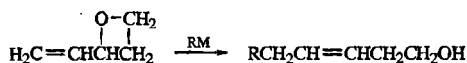
TL 36 7129 (1995)



JOC 51 5216 (1986)

X = H, CO₂R

TL 33 6169 (1992)

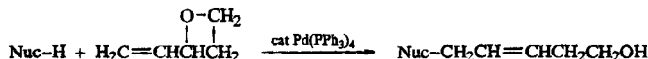
RM

RX (RX = ArI, vinylic I or OTf), cat Pd(OAc)₂, LiCl SL 145 (1993)
 or *n*-Bu₄NCl, NaO₂CH, *i*-Pr₂NEt

PhLi SL 341 (1990)

R₃B, O₂ SL 341 (1990)

RMgX (R = alkyl, allyl, aryl, vinylic), cat CuI SL 341 (1990)

R₂CuLi (R = alkyl, aryl, vinylic) SL 341 (1990)RHgCl (R = aryl, vinylic), cat Li₂PdCl₄, O₂, CuCl₂ TL 29 5069 (1988)

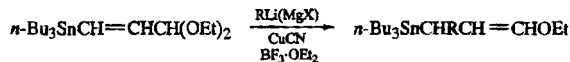
Nuc-H = H₂CXY (X, Y = COR, COR₂; CO₂R, CO₂R₂; CO₂R, CN),
 RCOCHR₂CO₂H (decarboxylation), R₂NH, ArOH, RCO₂H

TL 30 3487 (1989)

RM

RLi CC 34 (1984)
 JACS 113 8089 (1991)

RMgX, cat CuBr TL 3833 (1975)
 BSCF II 305 (1979)

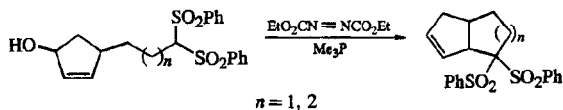
R₂C=CHAlR₂, cat Pd(PPh₃)₄ JOC 50 3406 (1985)PhZnCl, cat Pd(PPh₃)₄ JOC 50 3406 (1985)

JOC 59 7959 (1994)

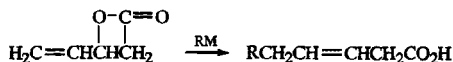
RM

RMgX, cat CuBr BSCF II 305 (1979)

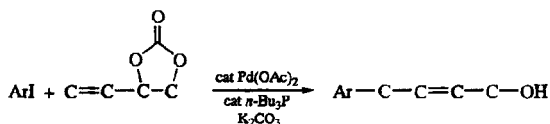
R₂C=CHAlR₂, cat Pd(PPh₃)₄, ZnCl₂ JOC 50 3406 (1985)PhZnCl, cat Pd(PPh₃)₄ JOC 50 3406 (1985)



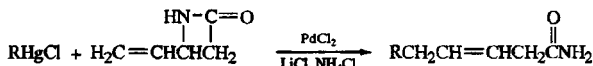
TL 36 8577 (1995)

RM

$\text{LiCR}_2\text{CS}_2\text{Me}$	CL 1901 (1983)
RMgX , cat CuI ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl; aryl; allylic, vinylic)	TL 22 1817 (1981) CL 1307 (1981); 71, 219 (1982)
R_2CuMgX ($\text{R} = 1^\circ$ alkyl, allylic, vinylic)	TL 22 1817 (1981) CL 1307 (1981); 71 (1982)
$\text{RC}(=\text{NNMe}_2)\text{CH}_2\text{Li}(\text{MgX})$, cat CuI	CL 1521 (1982)
$[\text{RC}(=\text{NNMe}_2)\text{CH}_2]_2\text{CuLi}(\text{MgX})$	CL 1521 (1982)

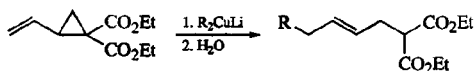


TL 36 8047 (1995)

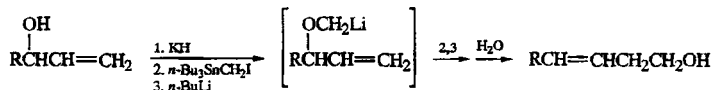


R = aryl, vinylic

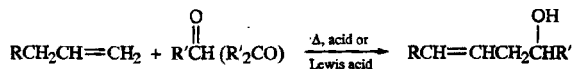
JOC 58 2081 (1993)



JOC 38 2100 (1973)



JACS 100 1927 (1978); 108 3841 (1986); 109 3017, 6199 (1987)
 TL 26 5013, 5017 (1985); 28 2099, 4993 (1987); 29 6901 (1988); 31 4301, 4425 (1990); 32 5401 (1991); 33 5795 (1992); 34 5217 (1993); 35 9021 (1994)
 JOC 52 2960 (1987)
 SL 845 (1992); 391 (1993); 228 (1994)
 See page 1063, Section 5, for the 2,3-Wittig rearrangement.



Reviews:

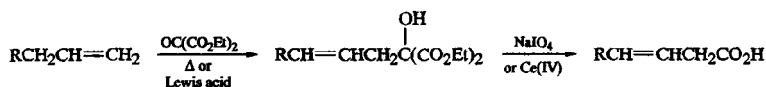
- Ann Chim 10 25 (1965)
 Angew Int 8 556 (1969)
 Syn 661 (1977)
 Acct Chem Res 13 426 (1980)
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
 Vol 2, Part 2.1, p 527
 SL 255 (1992) (asymmetric catalysis)

Intermolecular:

- JCS 4111 (1953)
 JACS 79 4972, 4976 (1957); 81 133 (1959); 104 555 (1982); 110 3585 (1988) (R' = CO₂R, chiral);
 111 1941 (1989) (R' = CO₂R, chiral); 112 3949 (R' = CO₂R, chiral Ti catalyst), 6737 (R' = CO₂R,
 Si effect), 7422 (H₂CO-Al complex), 8126 (1990); 114 6566 (1992) (R' = CO₂R, chiral Ti catalyst);
 115 3943 (H₂CO-Al complex), 7039 (on enol silanes, chiral catalyst, R' = CO₂R) (1993)
 Compt Rend C 263 153 (1966)
 JOC 33 1156 (1968); 37 964 (1972) (R' = CO₂R); 44 3567 (1982) (R' = CO₂R); 48 464 (1983); 50
 3025 (1985) (chiral); 51 4779 (1986) (R' = CO₂R); 54 2258 (1989); 56 2952 (1991) (R' = CO₂R);
 57 944, 5403, 6105 (R' = CO₂R), 7099, 7133 (chiral Ti catalyst, R' = CO₂R) (1992); 58 683
 (R' = CO₂R), 1030, 4189, 4287 (1993); 60 767 (1995)
 CC 380, 382 (1977) (both R' = CCl₃); 989 (1982) (R' = CO₂R)
 TL 4867 (1979) (R' = CCl₃); 1815 (1980); 28 5755 (1987); 29 3967 (chiral Al catalyst), 6305
 (R' = CO₂R) (1988); 30 4757 (1989); 31 2165, 3909 (α-amino RCHO) (1990); 32 743 (1991); 33
 1337 (chiral), 6695 (R' = CO₂R, chiral Ti catalyst), 7659 (chiral), 7701 (R' = CO₂R, chiral) (1992);
 34 477, 2409, 6281 (enol ethers and silanes), 7591 (chiral, R' = CF₃) (1993); 35 3133, 6693, 7793
 (all R' = CO₂R, chiral Ti catalyst), 7965 (1994); 36 1861 (1995) (R' = CO₂R, chiral Ti catalyst)
 Helv 64 1682 (1981)
 Tetr 42 2993 (1986) (R' = CO₂R)
 SL 29, 497 (lactol) (1993); 29 (chiral), 411 (R' = CO₂R, chiral), 1183 (1995)

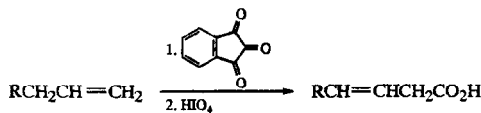
Intramolecular:

- Helv 50 153 (1967)
 TL 1219 (1967); 3325 (1973); 3783 (1977); 23 5111 (1982) (R' = CO₂R); 26 4167 (1985); 28 5945
 (1987); 29 1011 (1988); 30 1095 [Rh(I) catalyzed], 2465, 4849 [Rh(I) catalyzed] (1989); 31 2235,
 4641 (1990); 32 1107, 6571 (chiral Ti catalyst) (1991); 33 603 (SiO₂, high pressure), 7701 (1992);
 34 3571 (1993)
 JACS 89 2748 (1967); 94 4361 (1972); 103 1835 (1981); 105 7358 (1983); 106 718 (1984); 107 2730
 (1985); 109 4424 (1987); 111 2596 (1989); 112 2749, 9011 (organoaluminum promoted) (1990);
 113 2071, 5765 (1991); 117 193 (1995)
 JOC 35 186, 858 (1970); 42 1794 (1977); 44 4014 (1979); 45 4479 (1980); 47 745, 4538 (1982); 48
 1822 (1983); 50 4144 (1985); 52 5419 (1987); 53 4515, 6031 (1988); 56 5800 (1991); 57 2766,
 5851, 7133 (1992); 58 3912 (1993); 60 4146 (1995)
 CC 956 (1972)
 Syn Commun 8 449 (1978)
 Tetr 42 2951 (1986)
 SL 579, 857 (1991); 391 (1993); 337 (1994)

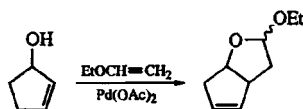


JACS 102 2473 (1980); 106 1092, 3797 (1984)

IOC 45 1228 (1980); 47 4201 (1982)

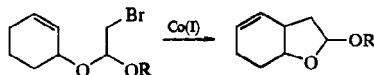


TL 23 1399 (1982)



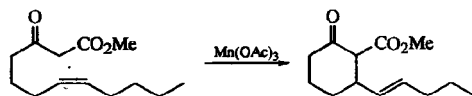
TL 30 2767 (1989)

JACS 111 9203 (1989); 113 7815 (1991)

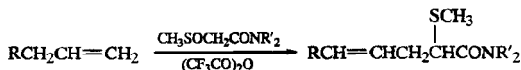


TL 25 4317 (1984)

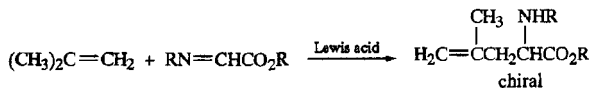
JOC 50 5875 (1985)



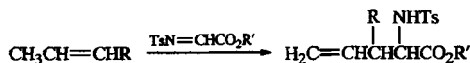
JOC 50 3659 (1985)



Syn 56 (1982)



TL 34 4841 (1993)

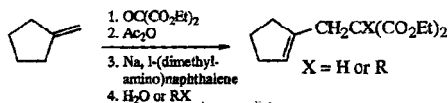


JCS Perkin I 2680 (1981)

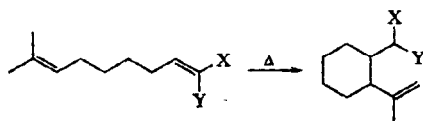
TL 23 3015 (1982)



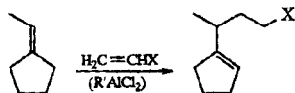
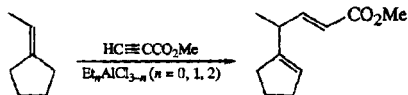
TL 29 3891 (1988)



TL 22 1885 (1981)

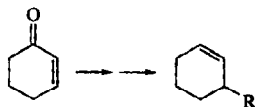
 $\text{X}, \text{Y} = \text{COR}, \text{COR}, \text{COR}, \text{CO}_2\text{R}; \text{CO}_2\text{R}, \text{CO}_2\text{R}; \text{CN}, \text{CO}_2\text{R}; \text{CN}, \text{CN}$

JOC 54 3120 (1989)

JOC 39 255 (1974) ($\text{X} = \text{CHO}, \text{COMe}, \text{CO}_2\text{Me}, \text{CN}$); 47 745 (1982) ($\text{X} = \text{CHO}, \text{COR}$)Helv 64 1682 (1981) ($\text{X} = \text{CO}_2\text{Me}$)JACS 104 1930 (1982) (α -substituted acrylate esters)TL 30 357 (1989) (intramolecular, $\text{X} = \text{CO}_2\text{R}$); 33 3343 (1992) [$\text{RCH}=\text{C}(\text{CN})\text{SOAr}$, intramolecular]

JOC 41 3061 (1976); 45 4773 (1980); 47 3921 (1982)

JACS 101 5283 (1979); 103 237, 1293 (1981); 104 2945 (1982)



See page 303, Section 54.3.

2. ELIMINATION

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol. 6, Parts 5.1–5.4, pp 949–1070

1. Dehydrogenation

Reviews:

P. N. Rylander, "Organic Synthesis with Noble Metal Catalysts," Academic Press (1973), Chpt 1
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 2.2, p 119



cat $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$, hv

CC 161 (1988)
 CL 263 (1988)
 JACS 111 7088 (1989)

cat $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$, hv, H_2 , alkene

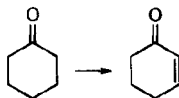
JACS 113 6706 (1991); 114 9492 (1992)

cat $\text{H}_2\text{Ir}(\text{O}_2\text{CCF}_3)(\text{PR}_3)_2$, Δ or hv

CC 1829 (1985)
 JACS 109 8025 (1987)

DDQ

JOC 53 3761 (1988)



DDQ

Chem Rev 67 153 (1967) (review)
 JOC 58 6807 (1993)

PdCl_2

JOC 36 752 (1971)
 J Prakt Chem 314 170 (1972)
 Syn 240 (1976); 773 (1977); 797 (1983)

PdCl_2 , $\text{Pd}(\text{OAc})_2$

JACS 105 2435 (1983)
 JOC 50 3957 (1985)

SeO₂, HOAcSeO₂, HOAc, HClSeO₂, HOAc, *t*-BuOHSeO₂, (PhSe)₂, MeOH/H₂O₂(PhSeO)₂O

JOC 58 1579 (1993); 59 7568 (1994)

JACS 110 6192 (1988)

Can J Chem 40 921 (1962)

JOC 57 2100 (1992)

JOC 58 3923 (1993)

CC 130 (1978); 1044 (1981)

JCS Perkin I 2209 (1980); 1947 (1982)

JACS 112 3252, 9001 (1990); 113 8130 (1991)

JOC 58 3877 (1993)

LDA/PhSe(O)Cl

JACS 113 4037 (1991); 114 9419 (1992)

PhSeCl/NaIO₄

JOC 58 1030 (1993)

PhSeCl/H₂O₂

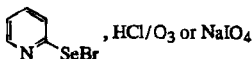
JACS 114 5959 (1992)

PhSeCl/*m*-ClC₆H₄CO₂H

JOC 59 6008 (1994)

PhSeCl, BF₃·OEt₂/H₂O₂

JOC 59 6395 (1994)

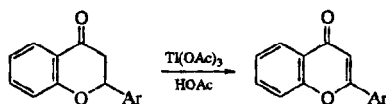
, HCl/O₃ or NaIO₄

TL 23 2105 (1982)

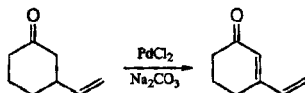
PhSeCl₃/NaHCO₃

JOC 53 4031 (1988)

See also page 287, Section 35.



TL 31 1459 (1990)



TL 32 4143 (1991)

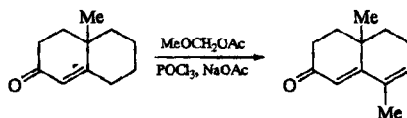
Na₂PdCl₄/base

Austral J Chem 33 1537 (1980)

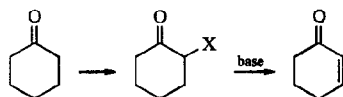
tetrachlorobenzoquinone

Can J Chem 62 2740 (1984)

JOC 54 3984 (1989)



Ann 712 (1983)

XBase

Cl

LiCl, DMF

JACS 75 4432 (1953)

TL 28 333 (1987)

JOC 60 2714 (1995)

LiBr, DMF

JACS 75 4432 (1953)

LiBr, Li₂CO₃, DMF

JACS 101 4003 (1979); 114

8375 (1992)

Syn Commun 11 7 (1981)

JOC 60 554, 1265 (1995)

Br

LiF, Li₂CO₃, HMPA

JOC 59 7709 (1994)

LiCl, DMF

TL 23 3405 (1982)

LiBr, Li₂CO₃, DMF

CL 3 (1973)

JOC 44 71 (1979); 52 4792

(1987); 59 2052 (1994)

JACS 106 3539 (1984); 111

3707 (1989)

CC 1319 (1986)

TL 34 4579 (1993)

LiBr, Li₂CO₃, CH₃CONMe₂

JACS 116 7658 (1994)

CaCO₃, CH₃CONMe₂

JCS 2532 (1961)

JOC 35 186 (1970); 51 3059

(1986)

KOH

JACS 108 4556 (1986)

collidine

JACS 72 362 (1950)

JOC 58 4871 (1993)

DBU

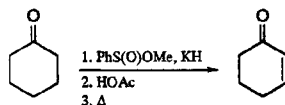
JOC 52 1962 (1987)

TL 28 503 (1987)

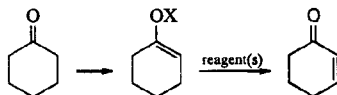
JACS 110 6192 (1988)

HMPA

TL 2105 (1968)

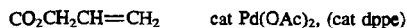


TL 36 7053 (1995)



See also page 287, Section 35.

<u>X</u>	<u>Reagent(s)</u>	
SiR ₃	NBS/DBU	JACS 110 6192 (1988)
	Pd(OAc) ₂	JACS 107 2474, 5495 (1985); 108 3841 (1986); 109 3017 (1987); 111 6257, 6287 (1989); 112 6959, 9436 (1990); 113 5378 (1991); 115 2992, 6078 (1993)
		IOC 52 3346, 4647 (1987); 55 555 (1990); 57 2100 (1992); 60 3318, 7837 (1995)
		SL 279 (1992)
		TL 36 7023 (1995)
	cat Pd-SiO ₂ , O ₂	CC 1697 (1989)
	cat Pd(OAc) ₂ , O ₂ , DMSO	TL 36 2423 (1995)
	cat Pd(OAc) ₂ , benzoquinone	IOC 43 1011 (1978); 51 4323, 5232 (1986); 52 5588 (1987); 59 2748 (1994)
		JACS 108 3443 (1986); 109 6199 (1987)
		TL 28 585 (1987); 36 7877 (1995)
		CL 1133 (1984)
		Tetr 42 2971 (1986)
	cat Pd(OAc) ₂ , H ₂ C=CHCH ₂ OCO ₂ Me, CH ₃ CN, (cat dppe)	
	cat Pd(OAc) ₂ -dppe (H ₂ C=CHCH ₂ O) ₂ CO, CH ₃ CN	TL 24 5635 (1983); 28 2397 (1987)
		Tetr 42 2971 (1986)
	SeO ₂	JACS 114 2560 (1992)
	PhSeCl/ <i>m</i> -ClC ₆ H ₄ CO ₂ H	JACS 107 268 (1985)
	PhSeCl/H ₂ O ₂	JACS 110 5568, 6192, 6558 (1988); 111 6287 (1989); 113 2610 (1991); 114 2560 (1992)
	PhSeCl/O ₃	JACS 115 2064 (1993)
	[PhSeSe(Me)Ph]BF ₄ ⁺ / <i>m</i> -ClC ₆ H ₄ CO ₂ H	JACS 112 4357 (1990)
	CAN	TL 36 3985 (1995)
	DDQ	TL 3455 (1978); 28 31, 4943 (1987)
		Syn 736 (1979)
		JOC 50 2981 (1985); 54 6118 (1989)
		JACS 110 5064 (1988); 112 9284 (1990); 114 7375 (1992)
	PhIO, Me ₃ SiN ₃ / <i>n</i> -Bu ₄ NF	TL 33 2933 (1992)
	¹ O ₂ /PPh ₃	Angew 16 413 (1977)
		JOC 60 7837 (1995)
	<i>t</i> -BuO ₂ H, cat CuCl ₂	JOC 58 678 (1993)
	(Ph ₃ C)BF ₄	JOC 42 3961 (1977)
		Syn 736 (1979)
Ac	cat Pd(OAc) ₂ , H ₂ C=CHCH ₂ OCO ₂ Me, <i>n</i> -Bu ₃ SnOMe, CH ₃ CN, (cat dppe)	TL 24 5635 (1983)
		CL 1133 (1984)
		Tetr 42 2971 (1986)

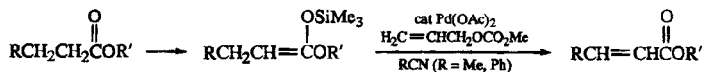


TL 24 1797 (1983)

CL 1133 (1984)

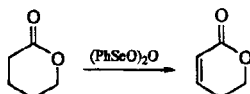
Acct Chem Res 20 140 (1987)

(review)



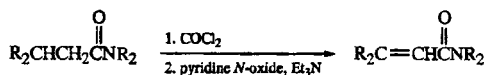
TL 25 4783 (1984)

Tetr 42 2971 (1986)

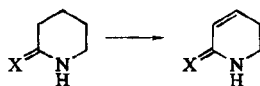


JCS Perkin I 1919 (1982)

JACS 113 2610 (1991)



JACS 101 4381 (1979)

X

O

Reagent(s)

PhS(O)OMe, KH / Δ

(PhSeO)₂O

DDQ,

CF₃C(OSiMe₃)=NSiMe₃

TL 36 7051 (1995)

JOC 46 1442 (1981)

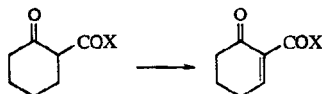
JACS 110 3318 (1988)

JOC 60 5337 (1995)

S

p-TolSOCl, *i*-Pr₂NEt / H₂O,
HOAc

JACS 108 212 (1986)

X

OR

Reagent(s)

DDQ

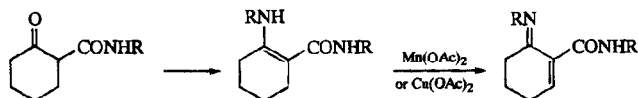
Pb(OAc)₄, cat Cu(OAc)₂

JACS 114 7375 (1992)

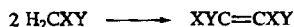
TL 34 3021 (1993)

NR₂Pb(OAc)₄, cat Cu(OAc)₂

TL 34 3021 (1993)



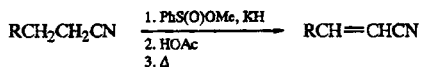
TL 34 5583 (1993)

Reagent(s)X, YCe(NO₃)-6H₂O, electrolysisCOR, COR
COR, CO₂R
CO₂R, CO₂R
CO₂R, CN

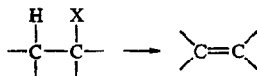
TL 36 8757 (1995)

Cl₃CB₃, DBUAr, CN
CO₂R, CO₂R

CL 73 (1978)



TL 36 7051 (1995)

2. Dehydrohalogenation of Alkyl HalidesReviews:

Chem Rev 45 347 (1949); 80 453 (1980)

Houben-Weyl, "Methoden der Organischen Chemie," Vol V/1b, pp 9-44, 134-180

Acct Chem Res 12 198, 430 (1979)

DMF

JACS 86 2309 (1964)

HMPA

CC 113 (1971)

Syn 885 (1984)

HMPA, microwave irradiation

JOC 60 2456 (1995)

Li₂CO₃

JOC 58 5797 (1993)

LiF, Li₂CO₃, HMPA

JOC 51 3407 (1986)

LiCl, DMF


SL 533 (1995)

KF-alumina

BCSJ 56 1885 (1983)

AgF, py

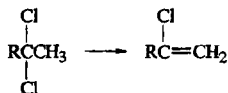
JOC 53 5046 (1988); 54 3764 (1989)

AgO_2CCF_3	JOC 56 3988 (1991)
Ag_2O	Helv 34 1176 (1951)
NaOAc	Org Syn Coll Vol 3 125 (1955)
$\text{NaOH}, (n\text{-Bu}_4\text{N})\text{HSO}_4$	Syn 688 (1979)
$\text{NaOH}, \text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	JOC 47 2493 (1982)
$\text{NaO-}i\text{-Pr}$, triglyme	Org Syn Coll Vol 5 285 (1973)
$\text{KOH}, \text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	Helv 60 3060 (1977) JOC 47 2493 (1982) JACS 114 3044 (1992)
KOH , cat $n\text{-Bu}_4\text{NBr}$, ultrasound	SL 893 (1992)
KOR	JACS 75 4112 (1953); 78 2199, 2203 (1956); 88 1425 (1966) Helv 60 3060 (1977) Coll Czech Chem Commun 46 833, 850 (1981) JOC 55 5247 (1990)
KOR, 18-crown-6	JOC 55 5247 (1990)
KO- <i>t</i> -Bu, <i>t</i> -BuOH	JOC 55 891 (1990)
KO- <i>t</i> -Bu, ether	JOC 57 6431 (1992)
KO- <i>t</i> -Bu, DMSO	JOC 30 2054 (1964); 32 510 (1967); 52 5218 (1987); 58 502 (1993); 56 6176 (1991); 57 701 (1992); 58 2501 (1993) JOC USSR 15 853 (1979); 18 71 (1982) JACS 108 468, 1251 (1986); 110 8223 (1988)
KO- <i>t</i> -Bu, 18-crown-6	Syn 372 (1979)
KO- <i>t</i> -Bu, Aliquat 336	TL 32 1539 (1991)
KO- <i>t</i> -Bu-Chromosorb W	Tetr 42 1575 (1986)
	JOC 45 900 (1980)
chiral LiNRR'	TL 28 5517 (1987)
LiNEt_2	Organomet Chem Syn 1 375 (1972)
LiNCy_2	JOC 32 510 (1967); 60 5319 (1995)
$\text{NaN}(\text{SiMe}_3)_2$	JOC 54 3334 (1989)
Et_3N	Org Syn 45 22 (1965)
PhNH_2	J Gen Chem USSR 25 2017 (1955)
PhNMe_2	Helv 40 130 (1957)

pyridine	Org Syn Coll Vol 4 980 (1963)
collidine	Ann 585 132 (1954)
quinoline	Rec Trav Chim 69 535 (1950) Org Syn Coll Vol 4 608 (1963) Org Syn 51 115 (1971)
DBN	Ber 99 2012 (1966) Angew 79 53 (1967) TL 2543 (1977) JOC 47 4358 (1982); 52 5624 (1987)
DBU	Angew 79 53 (1967) Syn 591 (1972) TL 2543 (1977); 36 1817 (1995) JOC 47 1944, 4358 (1982); 52 5067 (1987); 53 3912, 5909 (1988); 54 1468, 3091 (1989); 55 103, 1169 (1990); 59 7164 (1994) JCS Perkin I 2379 (1982) (polyene) JACS 110 854 (1988)
DBU, $\text{NiCl}_2(\text{PPh}_3)_2$ - PPh_3 - n -BuLi	CC 1621 (1986) (1° RX \rightarrow terminal alkene, X = Br, I) JOC 54 3015 (1989)
i -Pr ₂ NEt	Ber 91 380 (1958)
Cy ₂ NEt	Ber 91 380 (1958)
Ph ₃ CLi	JCS Perkin I 1820 (1980)
C ₈ K	JOC 54 2307 (1989)
Mg or Li/NiCl ₂ , H ₂ C=CH ₂	Ber 113 171 (1980)
m -ClC ₆ H ₄ CO ₃ H (X = I)	JACS 100 4888 (1978)
$\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \\ \diagup \\ \text{CH}_3 \end{array}$ (X = I)	JACS 117 3272 (1995)

For elimination via selenoxides, see page 287, Section 35.

3. 1,1-Dihalides

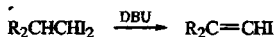


KOH

JACS 62 1367 (1940)

NaOEt

Org Mag Res 10 192 (1977)



TL 33 2043 (1992)



Compt Rend II 294 37 (1982)



Mg

JACS 108 1265 (1986)

Al, cat Cp_2TiCl_2

SL 489 (1991)

 $LiAlH_4$, $TiCl_3$ or $TiCl_4$

Syn 607 (1976)

 $LiAlH_4$, $CrCl_3$

TL 3829 (1977)

cat $Co(II)salen$, electrolysis

TL 34 809 (1993)

ii

JOC 48 4904 (1983)

at $Pd(PPh_3)_4$, $(ClMe_2Si)_2$

CL 613 (1982)

Cu

JOC 55 329 (1990)

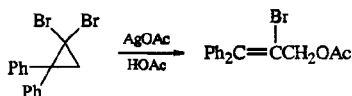
CuCl

Tetr 25 3461 (1969)

Zn-Cu

Syn 652 (1970)

JACS 106 8174 (1984)



Org Syn Coll Vol 6 187 (1988)

4. 1,2-Dihalides



X = Cl, Br

JOC 52 1145 (1987)

BaseX, Y

NaOMe, MeOH

F, Br

J Fluorine Chem 32 441 (1986)

NaOR, $NaNH_2$

Br, Cl

JOC 48 876 (1983)

Br, Br

JOC 45 5394 (1980)

NaO-*n*-Bu, $NaNH_2$

Cl, F

JOC 52 5494 (1987)

Cl, Cl

JOC 59 1930 (1994)

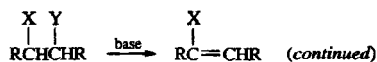
Cl, Br

JACS 101 228 (1979)

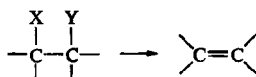
Br, Cl

JACS 101 228 (1979)

TL 24 2737 (1983)

BaseX, Y

	Br, Br	CC 1289 (1972) Tetr 30 1289 (1974)
KO- <i>t</i> -Bu	F, Br Cl, Cl Br, Br	J Fluorine Chem 32 441 (1986) JOC 55 3412 (1990) JACS 114 5018 (1992)
KOCHPhCHMeNR ₂ (enantioselective)	Br, Br	JOC 59 2285 (1994)
NaNH ₂	F, Br	J Fluorine Chem 32 441 (1986)



Review: Can J Chem 42 1294 (1964)

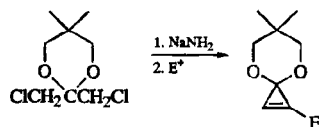
<u>Reagent(s)</u>	<u>X</u>	<u>Y</u>	<u>Stereochemistry of Elimination</u>	
Δ	Br	Br	anti	JOC 56 2582 (1991)
h ν , cat Ru(bipy) ₃ ²⁺ , Et ₃ N	Br	Br	?	JOC 55 2656 (1990)
h ν , cat Zn porphyrin, (HOCH ₂ CH ₂) ₃ N	Br	Br	?	JOC 53 1703 (1988)
electrolysis	Br	Br	anti	Coll Czech Chem Commun 28 1664 (1963) JOC 39 2408 (1974) Syn 964 (1979) TL 22 623 (1981)
Li	Br	Br	anti	TL 4269 (1968)
MeLi-glass	Cl	Cl	?	Tetr 42 1575 (1986)
	Br	Br	?	Tetr 42 1575 (1986)
<i>n</i> -BuLi	I	I	?	JACS 108 7121 (1986)
<i>i</i> -BuLi	Cl	Br	?	TL 29 5253 (1988)
	Br	Br	?	TL 23 5385 (1982) JOC 54 3519 (1989); 57 5959 (1992) JACS 113 7969 (1991) JOC 57 5959 (1992)
	I	I	?	
Na, <i>n</i> -BuOH	Cl	Cl	?	JOC 58 7498 (1993)

Na, NH ₃	Cl	Cl	?	TL 29 41 (1988) JACS 112 239 (1990); 117 9804 (1995) JOC 55 1506 (1990)
	Br	Br	nonstereospecific	JACS 74 4590 (1952)
	I	I	?	JACS 112 5633 (1990)
Na naphthalenide	Cl	Cl	?	JOC 52 3595 (1987)
	Br	Br	anti	JOC 37 507 (1972)
Mg	Br	Br	anti	JACS 74 4590 (1952) TL 4269 (1968)
NaBH ₄ , NiCl ₂	Br	Br	?	TL 26 4657 (1985)
Al, cat Cp ₂ TiCl ₂	Br	Br	anti	SL 489 (1991)
LiAlH ₄	Br	Br	anti	JACS 71 1675 (1949) Can J Chem 42 1294 (1964)
LiAlH ₄ , TiCl ₃ or TiCl ₄	Cl	Cl	?	Syn 607 (1976)
	Br	Br	?	Syn 607 (1976)
LiAlH ₄ , CrCl ₃	Br	Br	nonstereospecific	TL 3829 (1977)
SnCl ₂	Br	Br	nonstereospecific	JACS 92 4599 (1970)
SnCl ₂ , <i>i</i> -Bu ₂ AlH	Br	Br	?	CL 2069 (1984)
<i>n</i> -Bu ₃ SnH	Br	Br	nonstereospecific or anti	JACS 92 2849 (1970)
<i>o</i> -Me ₂ NCH ₂ C ₆ H ₄ - SnMe ₂ H	Br	Br	?	JOC 58 3046 (1993)
CrCl ₂	Br	Br	?	JACS 67 1728 (1945)
CrSO ₄	Cl	Cl	nonstereospecific	JACS 86 4603 (1964)
	Cl	I	nonstereospecific	JACS 86 4603 (1964)
	Br	Br	anti	JACS 86 4603 (1964)
Cr(ClO ₄) ₂ , EDA	Cl	Br	nonstereospecific	JACS 90 1582 (1968)
	Br	Br	anti	JACS 90 1582 (1968)
Fe graphite	Br	Br	anti	JOC 47 876 (1982)
(Et ₄ N)HFe ₃ (CO) ₁₁	Br	Br	?	JOMC 171 85 (1979)
Co(CN) ₅ ³⁻	Br	Br	?	JACS 87 5361 (1965)
NiBr ₂ (PPh ₃) ₂ , Zn, Et ₄ Ni (RCOCHCl- CHClCOR)	Cl	Cl	?	TL 26 3719 (1985)
Pd(PPh ₃) ₄	Br	Br	anti	BCSJ 52 3629 (1979)
cat Pd(PPh ₃) ₄ , (ClMe ₂ Si) ₂	Cl	Cl	?	CL 613 (1982)
	Br	Br	?	CL 613 (1982)

Reagent(s)	X	Y	Stereochemistry of Elimination	(continued)
Cu	Br	Br	nonstereospecific	JOC 27 4523 (1962)
CuCl	Br	Br	?	Tetr 25 3461 (1969)
Zn	F	Cl	?	JOC 59 1844 (1994)
	Cl	Cl	?	JOC 59 4332 (1994)
	Cl	Br	?	JOC 59 1844 (1994)
	Br	Br	anti or nonstereo- specific	JACS 63 22 (1941); 74 4590 (1952); 80 182 (1958); 87 838 (1965); 107 516 (1987)
				Org Syn Coll Vol 3 526 (1955)
				JOC 27 4523 (1962); 50 2356 (1985)
				TL 4269 (1968); 35 3349 (1994)
				BCSJ 52 1752 (1979)
Zn, ultrasound	Cl	Cl	?	JACS 112 6715 (1990)
Zn, H ₂ NCSNH ₂	Br	Br	?	Syn Commun 11 901 (1981)
Zn, cat TiCl ₄	Br	Br	anti	Syn 1025 (1982)
Zn, cat CuI	F	Cl	?	JOC 60 6289 (1995)
Zn-Cu	Br	Br	anti	JCS 3057 (1931)
				JACS 59 403 (1937); 106 5295 (1984)
NaI	Cl	Cl	nonstereospecific	JOC 27 4523 (1962)
	Cl	Br	syn	JOC 41 3284 (1976)
			nonstereospecific	JOC 27 4523 (1962)
	Cl	I	nonstereospecific	JOC 27 4523 (1962)
	Br	Br	?	JACS 72 362 (1950)
				JOC 30 1658 (1965)
			nonstereospecific	JOC 27 4523 (1962)
				JACS 92 4602 (1970)
			syn	JOC 41 3284 (1976)
			anti	JACS 87 838 (1965)
KI	Br	Br	anti	TL 4269 (1968)
H ₂ NCSNH ₂	Br	Br	anti	Chem Ind 1418 (1966)
				Ind J Chem B 14 65 (1976)
Na ₂ S·9H ₂ O	Cl	Cl	anti	Syn 879 (1981)
	Br	Br	anti	Syn 879 (1981)
NaSPh	Br	Br	?	J Prakt Chem 53 1 (1896) Ber 30 1799 (1897)

NaO ₂ SPh	Br	Br	?	<i>J Prakt Chem</i> 53 1 (1896) <i>Ber</i> 30 1799 (1897)
NaSCN	Br	Br	?	<i>Chem Ind</i> 1418 (1966)
Na ₂ Se	Cl	Cl	?	<i>JOC</i> 31 4292 (1966)
	Br	Br	?	<i>JOC</i> 31 4292 (1966)
	I	I	?	<i>JOC</i> 31 4292 (1966)
NaSeH	Br	Br	?	<i>Ind J Chem B</i> 19 812 (1980)
RSeNa (R = Me, Ph)	Cl	Br	syn	<i>TL</i> 21 1877 (1980)
	Cl	I	anti	<i>TL</i> 21 1877 (1980)
	Br	Br	anti	<i>TL</i> 21 1877 (1980)
Te, NaBH ₄	Br	Br	anti	<i>Syn</i> 311 (1978)
Ph ₂ Te	Br	Br	?	<i>TL</i> (15) 5 (1960)
cat ThTeNa, NaBH ₄	Br	Br	anti	<i>TL</i> 23 3601 (1982)
(Ph ₃ Sn) ₂ Te, CsF	Br	Br	anti	<i>TL</i> 31 6291 (1990)
PPh ₃	Br	Br	nonstereospecific	<i>JOC</i> 28 1353, 1521 (1963)
(Me ₂ N) ₃ P	Cl	Cl	?	<i>JOC</i> 57 5018 (1992)
	Cl	Br	?	<i>JOC</i> 57 5018 (1992)
	Cl	I	?	<i>JOC</i> 57 5018 (1992)
	Br	Br	?	<i>JOC</i> 57 5018 (1992)
Me ₂ C̄HNO ₂ , DMSO	Br	Br	?	<i>TL</i> 36 5801 (1995)

5. 1,3-Dihalides

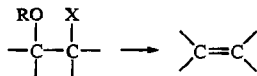


$\text{E}^+ = \text{NH}_4\text{Cl}, \text{RX}$

TL 32 1339 (1991)

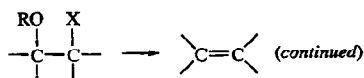
6. β -Halo Ethers

For other β -substituted ethers, see page 277, Section 20.



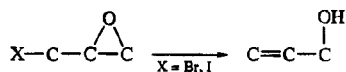
Stereochemistry of
Elimination

X	Reagent(s)		
Cl	Li, NH ₃	?	<i>JOC</i> 43 786 (1978); 45 48 (1980)

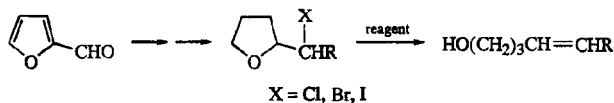


<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry of Elimination</u>	
	Li, (4- <i>t</i> -BuC ₆ H ₄) ₂	?	JACS 107 3271, 3279 (1985) JACS 107 3285 (1985); 115 7152 (1993)
	Na	?	JCS 1707 (1950) Ann 536, 1478 (1982) Org Syn Coll Vol 6 675 (1988)
	Na, EtNH ₂	?	JACS 107 516 (1985)
	Cr(ClO ₄) ₂	?	JACS 109 4752 (1987) JOC 57 4567 (1992); 58 7537 (1993)
	Sml ₂	nonstereospecific	TL 29 6517 (1988)
Cl, Br	Na or K	?	JCS Perkin I 595 (1978)
	NaC ₁₀ H ₈	?	JCS Perkin I 595 (1978)
	Zn, Ag-graphite	?	JOC 54 2307 (1989)
Br	electrolysis	?	TL 35 1409 (1994)
	Li	?	JOC 9 310 (1944)
	Na	nonstereospecific	Ber 43 2175 (1910) JACS 72 2120 (1950); 80 182 (1958); 104 1116 (1982); 114 5018 (1992) JCS 1707 (1950) CC 552 (1977) JOC 50 5465 (1985)
	Na(Hg)	?	JACS 52 651 (1930), 56 126 (1934)
	Mg	?	JACS 52 3396 (1930); 53 1505, 2427 (1931); 54 751 (1932); 55 3293 (1933); 80 182 (1958); 112 2749 (1990)
	Zn	nonstereospecific	JOC 17 807 (1952); 52 1803 (1987); 53 640 (1988); 60 5048 (1995) Org Syn Coll Vol 4 748 (1963) Helv 62 1990 (1979) TL 26 1123 (1985); 28 3839 (1987); 29 2727 (1988); 31 2229 (1990) CC 1462 (1987)
	Zn(Cu)	?	JACS 111 3728 (1989)
	Zn(Ag)	?	BCSJ 53 3383 (1980) JACS 104 1114 (1982); 105 1058 (1983)

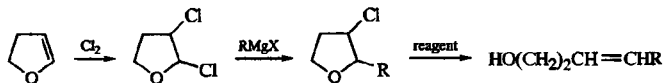
		JOC 50 3224 (1985); 52 598, 603 (1987)
		CC 1642 (1986)
Zn-Ag-graphite	?	JOC 56 2213 (1991)
<i>n</i> -BuLi	?	JACS 107 3271 (1985)
		TL 30 6737 (1989)
LiC ₁₀ H ₈	nonstereospecific	TL 31 1907 (1990)
NaC ₁₀ H ₈	nonstereospecific	TL 31 1907 (1990)
KC ₈	?	TL 31 3735 (1990)
Zn	?	TL 28 6497 (1987); 35 3621 (1994)
		JOC 54 2307 (1989); 57 3732, 5813 (1992); 58 6255 (1993); 60 7849, 7857 (1995)
		SL 285 (1995)
Zn, NH ₄ Cl	?	JACS 112 5583 (1990)
Zn, py	?	JOC 55 2771 (1990)
Zn-Ag-graphite	?	JOC 54 2307 (1989); 55 1363, 1423 (1990); 56 2213 (1991)
		TL 31 3735 (1990)
MeLi	?	JOC 58 4567 (1993); 60 169 (1995)
<i>n</i> -BuLi	anti	TL 30 6737 (1989); 31 1907 (1990)
<i>t</i> -BuLi	?	JACS 109 4390 (1987)
Me ₂ BBr, <i>n</i> -Bu ₄ NI	?	TL 28 5985 (1987)



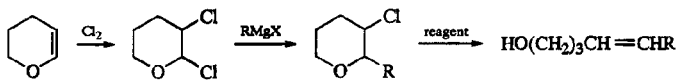
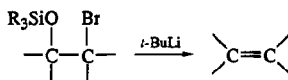
Zn, HOAc	Tetr 37 2581 (1981)
	JACS 109 6187 (1987); 112 260 (1990)
Zn, CuI, ultrasound	JOC 57 2757 (1992)
<i>n</i> -BuLi	JOC 56 5496 (1991)
<i>t</i> -BuLi	JACS 112 4552 (1990)
	SL 1007 (1992)

Reagent

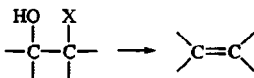
Na	BSCF 2 745 (1935); 10 484 (1943)
	Org Syn 25 84 (1945)
	JCS 1707 (1950)
Mg	JCS 195 (1936)
Me ₂ BBr, <i>n</i> -Bu ₄ NI	TL 28 5985 (1987)

Reagent

Na JCS 1152, 1714 (1950)

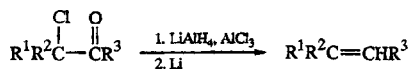
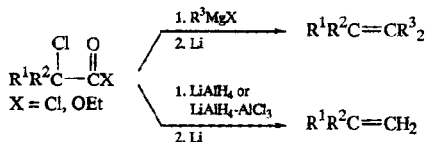
SmI₂ TL 29 6517 (1988)ReagentNa JCS 1707 (1950)
Ann 536, 1478 (1982)SmI₂ TL 29 6517 (1988)

Ber 115 1990 (1982)

7. Halohydrins

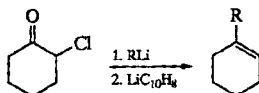
<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry of Elimination</u>	
Cl	Na, NH ₃	?	JACS 105 7358 (1983)
	<i>n</i> -BuLi / LiC ₁₀ H ₈	?	CC 1153 (1982)
	Al, cat PbBr ₂ , (HCl)	?	JOC 54 444 (1989)
	Cr(ClO ₄) ₂ , EDA	?	JACS 105 2435 (1983)
	electrolysis	?	Angew Int 16 57 (1977)
Br	TiCl ₃ , LiAlH ₄	nonstereospecific	JOC 43 3249 (1978)
	Cr(ClO ₄) ₂ , EDA	nonstereospecific	JACS 90 1582 (1968)
	Zn	?	JCS 1370 (1955)
	Zn, HOAc	?	JOC 53 863 (1988)
	Zn, EtOH	?	JACS 116 1776 (1994)
	Zn-Cu, EtOH	?	JACS 116 3125 (1994)
	(CF ₃ SO ₂) ₂ O, py/HMPA	anti	JACS 102 1433 (1980)
	KSCN/K ₂ CO ₃ /MeI	cis	TL 2709 (1975)
	KSeCN/K ₂ CO ₃	cis	TL 2709 (1975)

I	electrolysis SnCl ₂ , POCl ₃ , py	? anti	JOC 44 1404 (1979) JCS 112, 2539 (1959)
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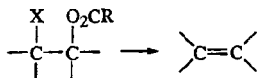
JOC 46 2721 (1981)

TL 30 5927 (1989)

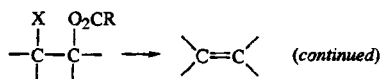


CC 1153 (1982)

J Chem Res (S) 128 (1985) (1,3-enynes)

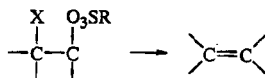
8. β -Halo Esters

<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry of Elimination</u>	
Cl	electrolysis	anti	Acta Chem Scand 17 2139 (1963)
Cl, Br	NaI	syn	JOC 44 1404 (1979); 45 154 (1980)
	Zn	anti or nonstereospecific	JACS 80 183 (1958); III 4829 (1989) JOC 44 1404 (1979); 45 154 (1980); 55 863 (1990) JCS Perkin I 1523, 1535 (1980) TL 36 7189 (1995)
Cl, Br, I	electrolysis	?	JACS 94 5139 (1972)
	Cr(OAc) ₂ , EDA	?	JOC 39 30 (1974)
Br	electrolysis	?	JOC 45 154 (1980)
	(Cp ₂ TiCl) ₂	?	JOC 60 7055 (1995)

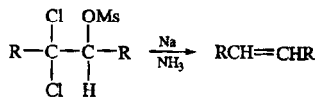


<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry of Elimination</u>	
	Cr(ClO ₄) ₂ , EDA	nonstereospecific	JACS 90 1582 (1968); 112 7413 (1990)
	Zn	?	JOC 53 640 (1988); 55 2823 (1990)
	Zn-Cu	?	TL 25 367 (1984); 31 3327 (1990)
	Zn / Ag-graphite	?	JOC 54 4780 (1989); 57 3473 (1992)
I	Zn	?	CC 1149 (1986)
	Zn, Ag-graphite	?	Acta Chem Scand B 36 251 (1982)
	NaI, Me ₃ SiCl / H ₂ O	anti	TL 27 3297 (1986); 31 6235 (1990)
			JOC 52 1051 (1987)
			JOC 54 2307 (1989)
			TL 25 2729 (1984)

9. β -Halo Sulfonates

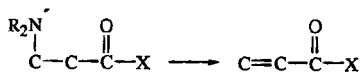


<u>X</u>	<u>Reagent(s)</u>	
Cl	Na, NH ₃	JOC 50 3957 (1985); 52 4772 (1987)
Br	Zn	TL 36 7957 (1995)
	Zn-Cu	JACS 81 1600 (1959)



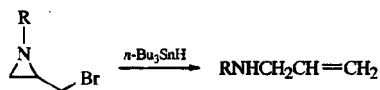
JOC 50 3957 (1985); 52 4772 (1987)

10. Amines



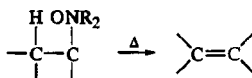
Reagent(s)	X	
SiO ₂	OR	TL 27 699 (1986) CC 1410 (1987) Tetr 44 4173 (1988) JOC 59 7994 (1994)
	NR ₂	
MeI/SiO ₂	OR	CC 1410 (1987)
MeI/DBN	OR	TL 3423 (1978) JOC 46 4536 (1981)
MeI/DBU	OR	CC 1112 (1983)
	NR ₂	JOC 59 7994 (1994)

11. β -Halo Amines



SL 287 (1994)

12. Amine Oxides (Cope Elimination)



JACS 81 2799 (1959); 108 1039 (1986)

Org Rxs 11 361 (1960) (review)

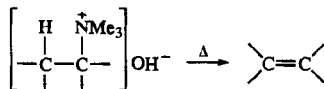
Org Syn Coll Vol 4 612 (1963)

JOC 55 4403 (1990)

TL 35 6673 (1994)

13. Quaternary Ammonium Salts

See also page 268, Section 10.

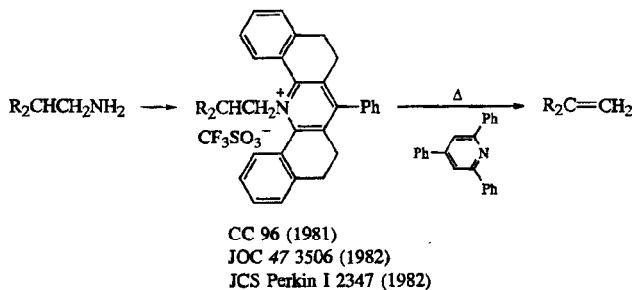


Org Rxs 11 317 (1960) (review)

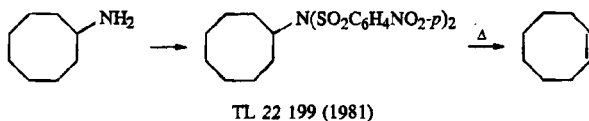
Org Syn Coll Vol 5 608 (1973); 6 552 (1988)

Org Syn 55 3 (1976)

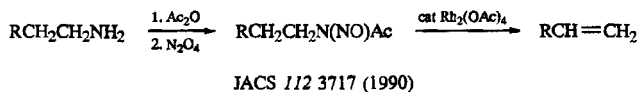
JACS 117 9804 (1995)



14. *N*-Alkyl-*N,N*-Disulfonimides

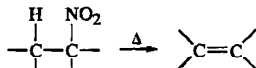


15. *N*-Nitrosocarboxamides

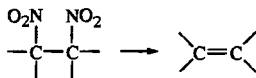


16. Nitro Compounds

See also page 285, Section 31.



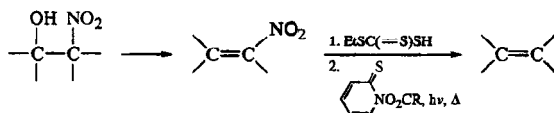
TL 29 2805 (1988)
 JOC 55 5801 (1990)



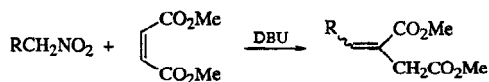
Na_2S JACS 93 4316 (1971)

NaSPh JACS 93 4316 (1971)

Ca(Hg) JOC 42 2944 (1977)

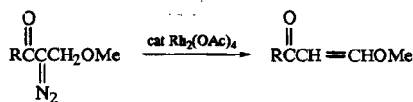


TL 34 8051 (1993)

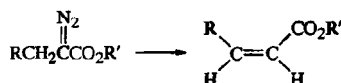


TL 35 9247 (1994)

17. Diazo Compounds



JOC 55 4767 (1990)



hv

TL 35 6709 (1994)

CF₃CO₂H

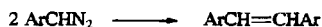
TL 35 6709 (1994)

cat Rh₂(OAc)₄

TL 22 4163 (1981); 35 6709 (1994)

Ag₂O

TL 35 6709 (1994)

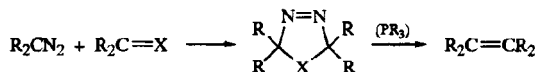


Rh catalyst

TL 23 2277 (1982)

cat (CF₃SO₂)₂O

TL 32 729 (1991)

X

S

JCS Perkin I 1794 (1974); 2079 (1976)

TL 1305 (1979); 22 4937 (1981)

Ber 117 277 (1984)

Tetr 42 1693 (1986)

JOC 55 1909 (1990)

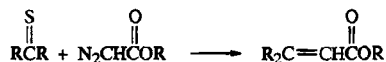
Se

JCS Perkin I 2079 (1976)

JOC 45 2890 (1980)

Ber 117 277 (1984)

See also page 305, Section 54.5.



JOC 54 2457 (1989)



X = R, OR

JACS 112 2003 (1990) (intramolecular); 115 30 (1993)

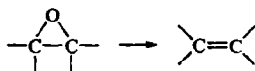
18. β -Substituted Azides



X = OC(S)SMc, PhSe

SL 454 (1994)

19. Ethers



Reviews:

Tetr 36 575 (1980)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 4.4, p 871

Inversion

LiCl, (CF₃CO)₂O / NaI

JOC 45 154 (1980)

JACS 111 636 (1989)

LiBr, (CF₃CO)₂O / NaI

JOC 45 154 (1980)

Ph₂PLi / HOAc, H₂O₂ / NaH

CC 142 (1974)

JACS 109 1248 (1987); 114 3044 (1992)

Ph₂PLi / MeI

JACS 93 4070 (1971); 95 822 (1973)

JOC 38 1178 (1973)



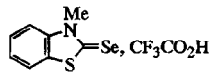
TL 28 3445 (1987)

Me₃SiSiMe₃, KOCH₃

JACS 98 1265 (1976)

JOC 41 3063 (1976)

CC 168 (1980)

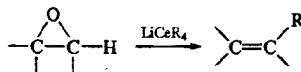
PhSiMe ₂ Li	Syn 199 (1976)
CpFe(CO) ₂ Na	JACS 94 7170 (1972) TL 4009 (1975)
NaBH ₂ S ₃ /LiAlH ₄ /PhCHO, H ⁺ /LiNR ₂	JCS Perkin I 433 (1974)
<u>Retention</u>	
Li	TL 21 1173 (1980)
Cp ₂ Nb	SL 465 (1990)
WCl ₆ , <i>n</i> -BuLi	JACS 94 6538 (1972) TL 1403 (1976) Can J Chem 57 3348 (1979) Org Syn 60 29 (1981) CC 1084, 1642 (1986) JOC 52 598 (1987) Org Syn Coll Vol 7 121 (1990) TL 36 1237 (1995)
WCl ₆ , Li or LiI	JACS 94 6538 (1972)
N ₂ C(CO ₂ Me) ₂ , cat Rh ₂ (O ₂ CR) ₄	TL 25 251 (1984); 32 6057 (1991) JOC 51 5503 (1986)
NaI, CF ₃ CO ₂ H	Chem Ind 712 (1984) JOC 56 4494 (1991)
NaI, (CF ₃ CO) ₂ O	JOC 43 1841 (1978)
NaI, 18-crown-6, BF ₃ ·OEt ₂	JOC 43 2076 (1978)
AlI ₃	TL 29 5815 (1988)
Me ₃ SiI	Nouv J Chim 3 705 (1979)
Me ₃ SiCl, NaI	TL 22 3551 (1981)
PI ₃ , (py or Et ₃ N)	Nouv J Chim 3 705 (1979)
P ₂ I ₄ , (py or Et ₃ N)	Syn 905 (1978) Nouv J Chim 3 705 (1979)
Ph ₃ P·HI, Ph ₃ PI ₂	Syn 828 (1980)
[(PhO) ₃ PCH ₃] ₂ , BF ₃ ·OEt ₂	JOC 43 2076 (1978)
KS ₂ CO- <i>n</i> -Bu	Chem Ind 460 (1964)
Ph ₃ PS, H ⁺ /Ph ₃ P	JACS 94 2880 (1972)
 Me N =Se, CF ₃ CO ₂ H	Syn 200 (1976)
Ph ₃ PSe, CF ₃ CO ₂ H	CC 253 (1973) TL 2091 (1974)
KSeCN	JCS Perkin I 1216 (1975) JOC 51 2712 (1986) TL 27 4813 (1986) JACS 110 1356 (1988)

RSeH (R = Me, Ph) / (CF ₃ CO) ₂ O or H ⁺ (EtO) ₂ PONa(Li), cat Te	TL 1385 (1976) CC 658 (1977) JOC 45 2347 (1980)
Te, LiHBEt ₃	JOC 59 1004 (1994)

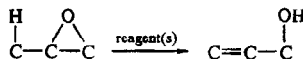
Nonstereospecific or Unknown Stereochemistry

NaI, <i>p</i> -TsOH	Chem Ind 524 (1983)
Mg(Hg), MgBr ₂	CC 144 (1970)
Et ₃ SiH, 300°C	JACS 109 7534 (1987)
Me ₃ SiLi	JACS 108 2090 (1986) (probably retention)
R ₃ P (R = <i>n</i> -Bu, Ph)	Chem Ind 330 (1959) JACS 87 2683 (1965)
(EtO) ₃ P	JOC 22 1118 (1957)
Ph ₃ PBr ₂ /Zn	JOC 41 3279 (1976)
KSCN or H ₂ NCSNH ₂ , H ⁺ / (EtO) ₃ P	JOC 26 3467 (1961)
H ₂ NCSNH ₂ , NaHCO ₃ / PPh ₃	CC 1434 (1987)
NaTeH / TsCl, py	TL 26 6197 (1985)
TiCl ₃ , LiAlH ₄	JOC 40 2555 (1975); 43 3249 (1978)
TiCl ₄ , Zn	JOC 43 3249 (1978)
Cp ₂ TiCl	JACS 112 6408 (1990); 116 986 (1994)
Cp ₂ MX ₂ , Na(Hg) [M = Ti, Zr ≫ Mo > W; X ₂ = Cl ₂ , O]	CC 99 (1978)
VCl ₃ (THF) ₃ , Zn	SL 510 (1992)
NbCl ₅ , NaAlH ₄	CL 157 (1982)
Cr	JOC 41 3647 (1976)
Cr(ClO ₄) ₂ , EDA	Tetr 24 3503 (1968)
WCl ₆ , LiAlH ₄	JOC 43 2477 (1978)
MeMnCl or <i>n</i> -Bu ₃ MnLi	TL 25 294 (1984)
Fe(CO) ₅ , Me ₂ NCONMe ₂	TL 4155 (1977)
FeCl ₃ , <i>n</i> -BuLi	CL 883 (1974)
cat (<i>n</i> -Bu ₄ N) ₂ [Fe ₄ S ₄ (SC ₆ H ₅) ₄], NaBH ₄	TL 30 6387 (1989)
Co ₂ (CO) ₈	CC 384 (1974)
MeLi, CuBr, <i>n</i> -Bu ₃ P	JACS 112 1286 (1990) (epoxy ketones)
Zn, HOAc	CC 1450 (1970)
Zn, NaI, HOAc, NaOAc	JCS 112, 2539 (1959) JOC 57 3454 (1992)

Zn, PPh ₃	TL 29 5767 (1988)
Zn-Cu, EtOH	JOC 36 1187 (1971)
SmI ₂	JACS 102 2693 (1980)
	TL 36 4963 (1995)
YbI ₂	JACS 102 2693 (1980)



TL 29 5165 (1988)



Reviews:

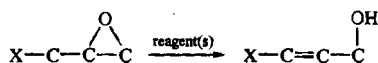
Russ Chem Rev 41 403 (1972)
 Tetr 39 2323 (1983)
 Org Rxs 29 345 (1983)
 Syn 629 (1984)

Reagent(s)

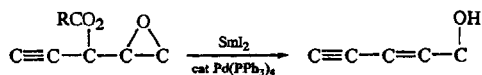
Li, EDA	Helv 50 153 (1967)
<i>n</i> -BuLi	TL 34 845 (1993)
<i>t</i> -BuLi	JACS 110 6558 (1988)
alkali metal amide bases	JACS 80 2849, 2855 (1958); 82 6370 (1960); 87 3125 (1965); 89 4526, 4527 (1967); 92 737, 2064 (1970); 95 5311 (1973); 106 2949 (1984); 108 3739 (1986); 110 1634 (1988)
	JOC 29 2830 (1964); 32 435, 532 (1967); 34 3583 (1969); 36 1365 (1971); 37 2060, 3919, 4250 (1972); 51 1362 (1986); 52 1907 (1987); 57 115 (1992)
	Syn 194 (1972); 602 (1975)
	Org Syn 53 17 (1974)
	TL 1929 (1974); 28 1439, 3831, 4993 (1987)
	Tetr 34 1541 (1978)
	Org Syn Coll Vol 6 948 (1988)
	SL 581 (1990)
	TL 31 4495 (1990)
LiNRR' (chiral)	JOC 45 755 (1980)
	CL 829 (1984); 389 (1987)
	TL 26 5803 (1985); 30 2125, 3377 (1989); 31 6703 (1990); 36 1893, 2847 (1995)
LDA, KO- <i>t</i> -Bu	JOC 59 4784 (1994)
CyN(<i>i</i> -Pr)MgBr	JACS 102 1433, 7986 (1980)
	JOC 51 793 (1986)

Reagent(s) (continued)

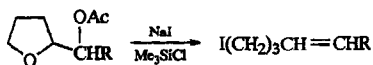
CyN(<i>i</i> -Pr)MgCH ₃	TL 27 299, 303 (1986) JACS 112 6429 (1990)
Et ₂ AlTMP	JACS 96 6513 (1974); 114 2567 (1992) Angew Int 17 169 (1978) BCSJ 52 1705 (1979) JOC 52 1106 (1987); 54 3515 (1989); 55 1589 (1990)
9-BBN-OTf, 2,6-lutidine	CL 1215 (1977)
AlCl ₃ , Et ₃ N, py	TL 35 7651 (1994)
Al(O- <i>i</i> -Pr) ₃	JOC 35 1598 (1978); 44 868 (1979); 50 2948 (1985); 56 4451 (1991) JCS Perkin I 2909 (1982) JACS 105 5510 (1983); 112 305 (1990) Helv 67 1998 (1984) CC 418, 727 (1986) SL 465 (1991) TL 34 8453 (1993)
Me ₃ SiOTf/DBU/HCl or HF	JACS 101 2738 (1979) Tetr 37 3899 (1981)
Me ₃ SiOTf/2,6-lutidine/ <i>n</i> -Bu ₄ NF	JACS 111 2596 (1989)
Et ₃ SiOTf/2,6-lutidine/H ₃ O ⁺	TL 28 6417 (1987)
Me ₃ SiBr, PPh ₃ /DBU/HCl	JACS 106 7854 (1984)
Me ₃ SiI/DBU or DBN/H ⁺	TL 21 2329 (1980) JOC 45 2579 (1980)
<i>t</i> -BuMe ₂ SiI/DBN/H ⁺	JOC 45 924 (1980)
(PhSe) ₂ , LiAlH ₄ / <i>m</i> -ClC ₆ H ₄ CO ₂ H	JOC 56 5401 (1991)
PhSeH, Ti(O- <i>i</i> -Pr) ₄ /H ₂ O ₂	JACS 110 6192 (1988)
Ti(O- <i>i</i> -Pr) ₄ (epoxy alcohols)	JACS 103 462 (1981)



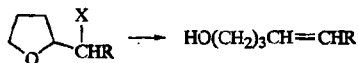
<u>X</u>	<u>Reagent(s)</u>	
Cl	LiNH ₂ or LDA	TL 31 4495 (1990)
OR	LDA, KO- <i>t</i> -Bu	SL 753, 803 (1992)
SR	electrolysis	TL 32 1099 (1991)
SOR	electrolysis NaOMe	TL 32 1099 (1991) Izv Akad Nauk SSSR, Ser Khim 1623 (1985)
SO ₂ R	electrolysis NaOMe	TL 32 1099 (1991) Izv Akad Nauk SSSR, Ser Khim 1623 (1985)



JACS 113 3873 (1991)



TL 32 3059 (1991)

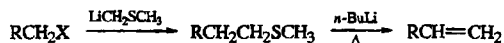
XReagent(s)

MsO

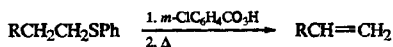
Na or Li, NH₃

Syn Commun 12 915 (1982)

PhS

LiC₁₀H₈Syn Commun 12 915 (1982)
TL 30 2537 (1989)**21. Sulfides**

JACS 101 3283 (1979)



JACS 112 5276 (1990)

cat (*p*-BrC₆H₄)₃N⁺ SbCl₆⁻

TL 30 4129 (1989)

PPh₃

JOC 23 1767 (1958)

TL 2861 (1975)

P(OEt)₃

JOC 23 1767 (1958); 26 3467 (1961)

TL 2861 (1975)

MeI

JOC 26 3467 (1961); 29 3258 (1964)

Li, EtNH₂

TL 24 1657 (1983)

RLi (R = *n*-Bu, Ph)

JOC 26 3467 (1961)

n-Bu₃SnH

TL 24 1657 (1983)

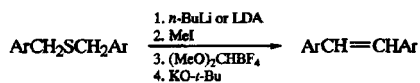
JOC 60 470 (1995)

n-Bu₃SnH, cat Et₃B

TL 35 6697 (1994)

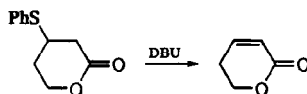
Raney Ni

TL 24 1657 (1983)



JOC 57 266 (1992)

JACS 117 1514 (1995)



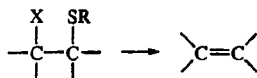
SL 594 (1994)



SL 628 (1995)

22. α -HalosulfidesX = Cl, Br; Y = H, Cl, Br; Z = CO₂R, COR, CN

Angew Int 20 585 (1981)

23. β -HalosulfidesXReagent(s)

F

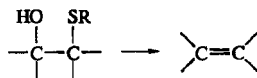
LiAlH₄, TiCl₄

TL 35 7783 (1994)

Cl

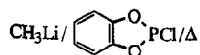
n-Bu₃SnH

TL 4223 (1977)

24. β -Hydroxysulfides*n*-BuLi/(PhCO)₂O/Li-NH₃ or NaC₁₀H₈

JACS 94 4758 (1972)

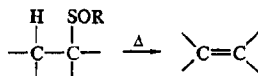
TL 27 1343 (1986)



TL 737 (1972)

base / CS ₂ / CH ₃ I / <i>n</i> -Bu ₃ SnH	TL 4223 (1977)
base / CS ₂ / CH ₃ I / <i>n</i> -Bu ₃ SnH, Et ₃ B	TL 29 6125 (1988)
electrolysis	TL 2807 (1978)
PI ₃ , P ₂ I ₄ or SOCl ₂	TL 4111 (1979)
$\left[\text{C}_6\text{H}_4\text{NEt}^+\text{F} \right] \text{BF}_4^-$, Et ₃ N/LiI	CL 413 (1978) JOC 45 3549 (1980)
$\left[\text{C}_6\text{H}_4\text{NMe}^+\text{F} \right] \text{BF}_4^-$, Et ₃ N/LiI, LiI·3H ₂ O or NaI	TL 29 659 (1988)
MsCl, py/LiI·3H ₂ O, Et ₃ N	TL 29 659 (1988)
TiCl ₄ /Zn	CL 37, 1161, 1523 (1974)
TiCl ₄ , LiAlH ₄ , R ₃ N	CL 871 (1975)

25. Sulfoxides



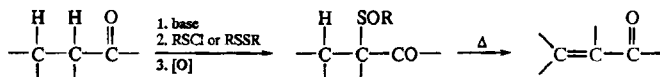
JOC USSR 18 395 (1982) (vinyl ethers)

JOC 52 1471 (1987); 53 2180 (1988); 54 4535 (1989); 55 5671 (1990); 56 723, 1329, 2317 (1991); 59 5414 (1994); 60 6180 (1995)

TL 28 221 (3,4-dihydrofuran), 3901 (vinyl fluorides), 4959, 5509 (α,β -unsaturated oxazolines) (1987); 30 6491 (1989); 31 5609 (1990); 35 5177 (1994)

JACS 112 4357 (1990); 113 2598, 5080 (1991)

SL 873 (1991)



JACS 95 6840 (1973); 98 4887 (1976); 106 721, 4038, 6414 (1984)

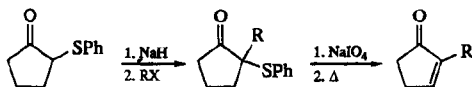
TL 5113 (1973); 1097 (1974); 4197 (1975); 29 4189 (1988); 31 2233 (1990); 34 5341 (1993)

Chem Rev 78 363 (1978)

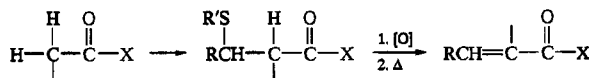
Acct Chem Res 11 453 (1978)

JOC 44 71 (1979); 50 2764 (1985); 52 1218 (1987) (on tosylhydrazone)

Syn 56 (1982)



JACS 108 3385 (1986)

X

R

TL 995, 2179 (1979); 29 1461 (1988)

Syn 1003 (1981)

Syn Commun 11 315 (1981)

RO

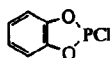
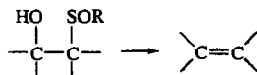
TL 993, 2179 (1979)



JACS 96 7165 (1974)

JOC 40 2014 (1975); 47 4801 (1982) (diene)

Syn Commun 9 317 (1979) (diene)

26. β -HydroxysulfoxidesNBS, NCS or SO_2Cl_2

TL 649 (1972)

JACS 95 3420 (1973)

27. Sulfones*n*-BuLi/cat $\text{Fe}(\text{acac})_3$

SL 215 (1994) (inter- and intramolecular)

n-BuLi or *i*-PrMgBr/cat $\text{Ni}(\text{acac})_2$

TL 23 2457 (1982)



TL 32 2565 (1991)

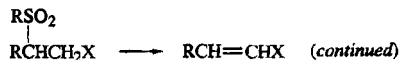
X

COR

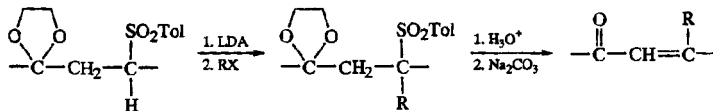
Reagent(s)basic Al_2O_3 Et_3N

TL 27 3733 (1986)

JACS 111 7487 (1989)

XReagent(s)

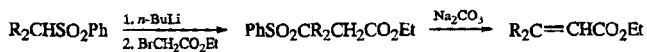
	DBU	CC 1226 (1987) TL 29 1461 (1988); 31 6685 (1990)
CO ₂ R	Et ₃ N DBU	TL 33 4065 (1992) TL 31 5575 (1990); 33 4065 (1992); 34 2945 (1993)
SO ₂ Ph	O ₂ , electrolysis	TL 36 2083 (1995)



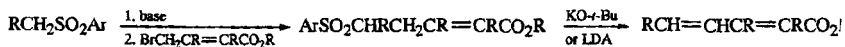
JOC 42 1349 (1977)
CL 165 (1982)



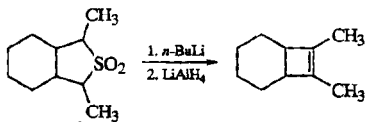
TL 30 6085 (1989)



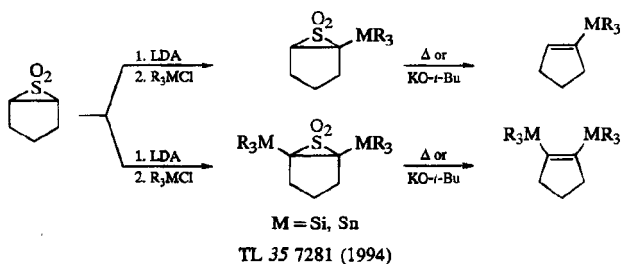
BSCF 525 (1976)



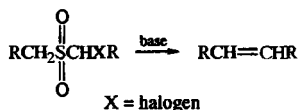
BSCF 746 (1973)
TL 27 3337 (1986)



Org Syn 57 53 (1977)
JACS 109 3730 (1987)
Org Syn Coll Vol 6 482 (1988)



28. α -Halosulfones (Ramberg-Bäcklund Reaction)



F. G. Bordwell in "Organosulfur Chemistry," Ed. M. J. Janssen, Interscience, New York (1967), Chpt 16 (review)

TL 4645 (1967); 29 4803 (1988); 30 3267 (1989); 36 7767 (1995)

Acct Chem Res 1 209 (1968) (review)

JACS 91 3870 (1969); 92 2581 (1970); 96 3332 (1972); 109 2857 (1987); 110 4866, 5479, 8197 (1988); 111 2652 (1989); 112 265 (1990); 113 9682 (1991); 114 7360 (1992); 117 1437 (1995)

Tetr 30 3177 (1974)

Org Rxns 25 1 (1977) (review)

Ber 114 909 (1981)

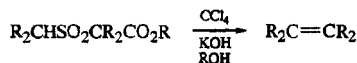
Syn 504 (1982) (phase transfer)

Ann 98 (1983)

JOC 51 2397 (1986); 52 1703 (1987)

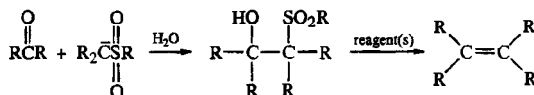
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 3.8, p 861 (review)

SL 660 (1993)



TL 36 8367 (1995)

29. β -Hydroxysulfones



Reagent(s)

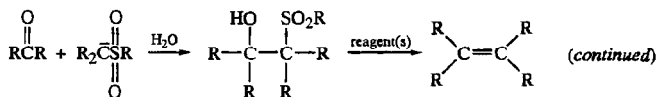
electrolysis

CL 69 (1978)

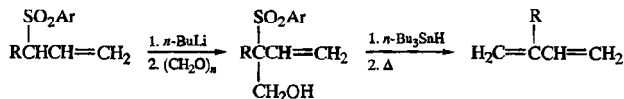
Na(Hg), MeOH

JOC 42 2036 (1977); 54 890 (1989)

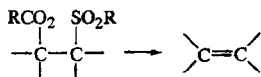
JCS Perkin I 829 (1978)

Reagent(s)

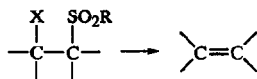
	TL 26 5597 (1985) JACS 110 4368 (1988)
Na(Hg), MeOH, Na ₂ HPO ₄ or KH ₂ PO ₄	JOC 50 5465 (1985); 52 3759 (1987); 54 4004 (1989); 59 1139 (1994); 60 6000 (1995) TL 27 2095 (1986); 34 6607, 7479 (1993) JACS 108 2776 (1986); 114 644 (1992)
<i>n</i> -BuLi/PhCSCl/ <i>n</i> -Bu ₃ SnH	TL 4223 (1977)
MsCl or TsCl/Na(Hg), MeOH	TL 4833 (1973); 23 1963 (1982); 26 5597 (1985); 30 4637 (1989); 32 495, 1149 (1991)
SOCl ₂ , py/Na(Hg), MeOH	JACS 108 2776 (1986)
SmI ₂	TL 31 7105 (1990) SL 859 (1994)



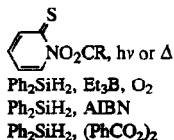
TL 22 2675 (1981)

30. β -Acyloxysulfones

Na, EtOH	JOC 50 2948 (1985)
Na(Hg), MeOH, (Na ₂ HPO ₄)	TL 4833 (1973); 4419 (1979); 27 3903, 6345 (1986); 28 5205, 5759, 5763 (1987); 30 4867 (1989) JCS Perkin I 829, 834 (1978); 1045, 1400 (1980) JOC 49 3503 (1984); 52 2838 (1987); 53 1064 (1988) JACS 107 2996 (1985); 108 284, 4603 (1986); 112 1626, 2003, 5276, 5290 (1990); 115 30 (1993) CC 479 (1986); 1342 (1987)
Na, NH ₃	JACS 113 6639 (1991)
Mg, cat HgCl ₂ , EtOH	TL 36 5607 (1995)
SmI ₂	TL 33 8065 (1992); 36 3523 (1995) SL 859 (1994) JOC 60 3194 (1995)

XReagent(s)

MeSC(S)O



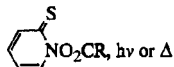
TL 32 2703 (1991)

TL 32 2703 (1991)

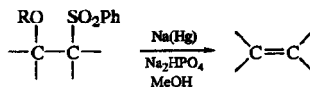
TL 32 2703 (1991)

TL 32 2703 (1991)

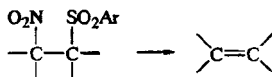
PhC(Se)O



TL 32 2703 (1991)

31. Other β -Substituted Sulfones

TL 36 5815 (1995)

*n*-Bu₃SnHTL 27 1595 (1986)
JOC 52 5111 (1987)
JACS 111 4829 (1989)

Na

BCSJ 53 3295 (1980)

Na₂SBCSJ 53 3295 (1980)
JOC 52 5111 (1987)

PhSNa

BCSJ 53 3295 (1980)

Na₂S₂O₄

BCSJ 53 3295 (1980)

NaTeH

JOC 52 5111 (1987)

Me₂C(Li)NO₂

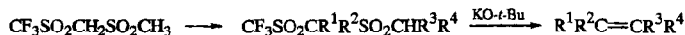
BCSJ 53 3295 (1980)



TL 23 2223 (1982); 31 6609 (1990); 32 531 (1991)

JOC 57 2471 (1992)

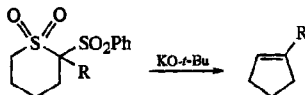
32. Disulfones



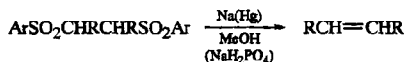
TL 25 4617 (1984)

JOC 50 2110 (1985)

JACS 108 2358 (1986)



JACS 112 8084 (1990)



CC 914 (1982)

TL 1653 (1983)

Phosphorus and Sulfur 14 229 (1983)

JOC 49 596 (1984); 50 4340 (1985); 52 3250, 4732, 4740 (1987)

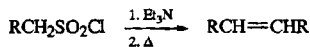
Can J Chem 62 2487 (1984)

JACS 107 4789, 6400 (1985); 108 3453 (1986); 110 6521 (1988); 111 2351 (1989); 112 1159 (1990)

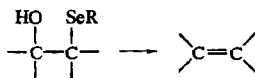
Tetr 42 1789 (1986)

SL 628 (1995)

33. Sulfonyl Halides



TL 30 3131 (1989)

34. β -Oxyselenides

TsOH

TL 1385, 3227, 3743 (1976)

HClO₄

TL 1385, 3743 (1976)

(CF₃CO)₂O, Et₃N

TL 1385, 3743 (1976)

MsCl, Et₃N

CC 790 (1975)

SOCl₂, Et₃N

TL 3227, 3743 (1976)

CC 564 (1982); 1540 (1987)

JOC 51 3108 (1986)

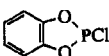
JCS Perkin I 413 (1989)

POCl₃, Et₃N

TL 2693 (1978)

PI₃, Et₃N

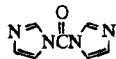
CC 1136 (1979); 565 (1982)

NaH/  PCl

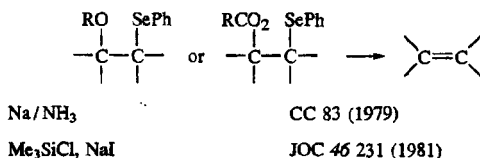
TL 3743 (1976)

Me₃SiCl, NaI

JOC 46 231 (1981)



CC 1136 (1979)



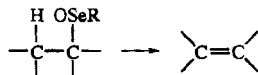
35. Selenoxides

See also page 231, Section 5.

Reviews:

Tetr 34 1049 (1978)

Acct Chem Res 12 22 (1979)



JOC 36 2561 (1971); 43 1697 (1978); 57 3887 (1992)

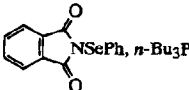
TL 1979 (1973); 1141 (1978); 22 1809 (1981); 27 2949 (1986); 28 1550, 4917, 5119 (1987); 32 777 (1991)

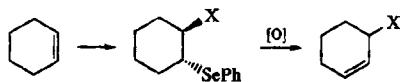
CC 1578 (1987)

JACS 115 5847 (1993) (chiral)

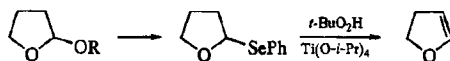
		$\text{RCH}_2\text{CH}_2\text{X} \xrightarrow{\text{Se reagent}} \text{RCH}_2\text{CH}_2\text{SeR}' \xrightarrow{[\text{O}]} \text{RCH}=\text{CH}_2$	
X	Se Reagent	Oxidant	
Br	NaSePh	H ₂ O ₂	JOC 52 2337 (1987)
	<i>o</i> -NO ₂ C ₆ H ₄ SeCN, NaBH ₄	H ₂ O ₂	JOC 40 947 (1975); 60 5224 (1995)
OH	<i>o</i> -NO ₂ C ₆ H ₄ SeCN, <i>n</i> -Bu ₃ P	H ₂ O ₂	JOC 41 1485 (1976); 58 832 (1993); 60 794 (1995) JACS 105 6723 (1983); 106 4186, 5335 (1984); 108 468, 1019 (1986); 112 2749 (1990); 115 3146 (1993)



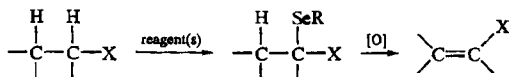
<u>X</u>	<u>Se Reagent</u>	<u>Oxidant</u>	
		H_2O_2	TL 27 4813 (1986); 28 3061 (1987); 29 4073 (1988) IOC 46 1215 (1981); 60 1856 (1995)
OMs	NaSePh	KIO_4	TL 28 3671 (1987)
	<i>o</i> -NO ₂ C ₆ H ₄ SeCN, NaBH ₄	H_2O_2	JACS 98 1612 (1976)
	NaBH ₃ SePh	H_2O_2	JACS 113 6621 (1991)
	(PhSe) ₂ , LiAlH ₄	H_2O_2	IOC 56 2161 (1991)



IOC 39 428, 429 (1974)



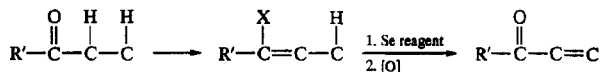
TL 35 5513 (1994)



Review: Org Rxns 44 1 (1993)

<u>X</u>	<u>Reagent(s)</u>	
CHO	(PhSe) ₂ , SeO ₂ , H ₂ SO ₄	TL 23 4813 (1982)
COR	PhSeX (X = Cl, Br)	JACS 95 6137 (1973) IOC 50 2981 (1985) TL 28 5755 (1987)
	(PhSe) ₂ , SeO ₂ , H ₂ SO ₄	TL 23 4813 (1982)
	KH/(PhSe) ₂	IOC 59 885 (1994)
	LiNR ₂ /PhSeX (X = Cl, Br)	JACS 95 5813 (1973); 97 5434 (1975); 107 7745 (1985); 108 3443 (1986); 112 239 (1990); 115 3056 (1993) IOC 39 2133 (1974); 47 1598 (1982); 51 2416, 5232 (1986); 54 3988 (1989); 58 2468 (1993); 59 885 (1994) Tetr 37 3981 (1981) TL 28 6021 (1987)

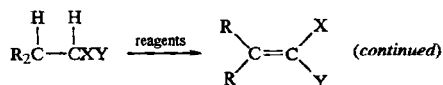
CO ₂ R	LDA / PhSeX (X = Cl, Br)	JACS 95 5813, 6137 (1973); 97 5434 (1975); 114 7387 (1992) JOC 39 2133 (1974); 52 2639 (1987)
lactone	LDA / PhSeX (X = Cl, Br)	JACS 97 5434 (1975) JOC 51 4836 (1986); 58 4127 (1993)
	LDA / (PhSe) ₂	JOC 39 120 (1974); 43 3693 (1978); 52 4792 (1987); 54 1952 (1989); 58 322 (1993)
CN	LiNR ₂ / PhSeX (X = Br, OAc) or (PhSe) ₂	TL 2279 (1974)
PhSO ₂	<i>n</i> -BuLi / PhSeCl	TL 28 5763 (1987)
NO ₂	<i>n</i> -BuLi / PhSeBr	JOC 58 3850 (1993)



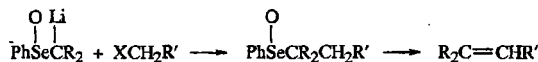
<u>X</u>	<u>Se reagent</u>	
NR ₂ (R' = H)	PhSeCl	TL 21 4417 (1980)
OAc	PhSeO ₂ CCF ₃	CC 695 (1973) JACS 97 5434 (1975)
	MeLi / PhSeBr	JOC 39 2133 (1974)
	PhSeCl, <i>n</i> -Bu ₄ NF	CC 880 (1987)



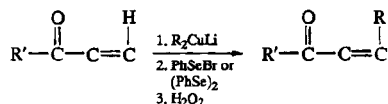
<u>X</u>	<u>Y</u>	<u>Reagents</u>	
CHO	COR	PhSeCl, py / H ₂ O ₂	JOC 46 2920 (1981)
COR	COR	PhSeCl, py / H ₂ O ₂	JOC 46 2920 (1981)
		NaH / PhSeCl / H ₂ O ₂	Org Syn Coll Vol 6 23 (1988)
		NaH / PhSeCl(Br) / H ₂ O ₂ , O ₃ or <i>m</i> -ClC ₆ H ₄ CO ₂ H	JACS 97 5434 (1975)
		LDA / PhSeCl(Br) / H ₂ O ₂ or O ₃	JOC 39 2133 (1974)
		NaH / Se / MeI / H ₂ O ₂ or <i>m</i> -ClC ₆ H ₄ CO ₂ H	TL 22 3043 (1981)
		(PhSe) ₂ , SeO ₂ , H ₂ SO ₄ / ?	TL 23 4813 (1982)
COR	SOR	NaH / PhSeCl(Br) / H ₂ O ₂	JACS 97 5434 (1975) Org Syn Coll Vol 6 23 (1988)
COR	CO ₂ R	PhSeCl, py / H ₂ O ₂	JOC 46 2920 (1981)
		NaH / PhSeCl(Br) / H ₂ O ₂	JACS 97 5434 (1975); 113 381 (1991) Org Syn Coll Vol 6 23 (1988)
		NaH or LDA / PhSeCl(Br) / H ₂ O ₂ or O ₃	JOC 39 2133 (1974)
		NaH / Se / MeI / H ₂ O ₂	TL 22 3043 (1981)
		(PhSe) ₂ , SeO ₂ , H ₂ SO ₄ / ?	TL 23 4813 (1982)



<u>X</u>	<u>Y</u>	<u>Reagents</u>	
COR	CONR ₂	KN(SiMe ₃) ₂ / PhSeCl / m-ClC ₆ H ₄ CO ₃ H	TL 27 2691 (1986)
CO ₂ R	CO ₂ R	PhSeCl, py / H ₂ O ₂ NaH / Se / MeI / H ₂ O ₂	JOC 46 2920 (1981) TL 22 3043 (1981)



IACS 97 3250 (1975)

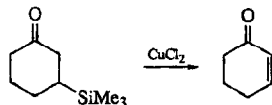


JOC 39 2133 (1974); 50 2539 (1985)

JACS 97 5434 (1975); 108 6276 (1986)

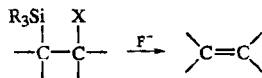
36. Tellurides

CL 447 (1981)

37. Organosilanes

Tetr 44 4757 (1988)

TL 30 7075 (1989); 31 4759 (1990)

38. β -Halosilanes

TL 23 3455 (1982); 36 3457 (1995)

Tetr 42 1575 (1986)

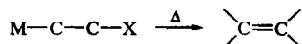
Angew Int 28 1711 (1989)

JACS 113 5084, 7980 (1991); 116 6463 (1994)

JOC 59 8125 (1994)

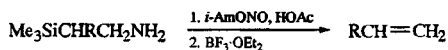
39. β -Oxysilanes and -Stannanes

See also page 337, Section 14 and page 341, Section 16.



<u>M</u>	<u>X</u>	<u>Reagent</u>	
SiR_3	OH	Δ	JCS Perkin II 1703 (1991) JOC 59 1925 (1994)
	OR	Δ	JACS 110 2611 (1988) JOC 59 1925 (1994)
	O_2CCF_3	Δ	JOC 59 1925 (1994)
	OMs	Δ	JOC 41 1966 (1976)
SnR_3	OH	Δ	Ber 115 1818 (1982) CC 739 (1992)
		H^+	Ber 115 1818 (1982)
	O_2CR	Δ	Organomet 11 3910 (1992)
SnR_2X (X = Cl, O_2CR , acac)	OR	Δ	JOMC 450 97 (1993)
	O_2CR	Δ	JOMC 450 97 (1993)

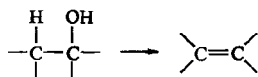
40. β -Aminosilanes



JOC 55 4474 (1990)


41. Dehydration of Alcohols

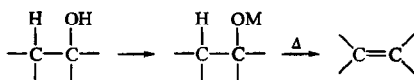
For the elimination of 3-hydroxyalkanoic acids, see page 309, Section 56.



DMSO	JOC 27 2377 (1962); 29 123, 221 (1964); 58 7899 (1993) TL 28 1175 (1987)
HMPA	TL 567 (1971); 165 (1972); 26 2275 (1985); 29 2537 (1988) JOC 36 3826 (1971) BCSJ 47 1693 (1974) JACS 107 4786 (1985); 111 2169 (1989)
H-montmorillonite	TL 34 1185 (1993)

HBr	Org Syn Coll Vol 3 312 (1955)
H ₂ SO ₄	Org Syn Coll Vol 1 183, 430 (1941); 2 606 (1943); 4 771 (1963)
H ₃ PO ₄	Org Syn Coll Vol 2 151 (1943) JOC 50 2179 (1985)
P ₂ O ₅	JACS 69 2022 (1947) JCS 2154 (1954)
(CO ₂ H) ₂	JACS 69 50 (1947) JCS 2154 (1954)
<i>p</i> -TsOH	JOC 52 5574 (1987); 53 893 (1988)
<i>p</i> -TsOH, silica	Syn 1159 (1985)
NaHSO ₄	JACS 69 2022 (1947)
KHSO ₄	JACS 69 2022 (1947); 109 7122 (1987) Gazz Chim Ital 112 231 (1982) JOC 53 4555 (1988); 59 1855 (1994)
BF ₃ ·OEt ₂	JACS 108 3835 (1986) TL 32 6489 (1991)
CuSO ₄	Acta Chem Scand B 31 721 (1977) JOC 45 917 (1980); 47 2590 (1982)
CuSO ₄ -silica gel	TL 28 4565 (1987); 31 3941 (1990)
I ₂	JCS 588 (1947) JOC 60 3448 (1995)
I ₂ , Ph ₃ BiBr ₂	TL 35 5035 (1994)
FeCl ₃ , SiO ₂	JOC 43 1020 (1978)
KOH	JACS 69 2022 (1947); 70 1646 (1948) Ber 93 2591 (1960)
Al ₂ O ₃ , Δ	Org Syn Coll Vol 3 312 (1955)
ThO ₂ , Δ	JACS 85 2180 (1963)
NBS, py	Chem Rev 63 21 (1963)
(PhO) ₃ PBr ₂ /K ₂ CO ₃	JCS Perkin I 1136 (1980)
[(PhO) ₃ PMe]I, HMPA	JOC 37 4190 (1972); 52 2644 (1987); 53 860 (1988)
POCl ₃ , py	JACS 83 5003 (1961); 106 6690 (1984); 107 4964 (1985); 108 3443 (1986) JOC 60 2748 (1995)
POCl ₃ , HMPA	JACS 102 7910 (1980)
SOCl ₂ , py	JACS 77 1028 (1955); 110 497 (1988) JCS Perkin I 1136 (1980) JOC 51 5463 (1986); 53 901 (1988); 55 1569 (1990) TL 31 5617 (1990)

MsCl, DMAP	TL 31 3325 (1990)
Tf ₂ O, py	JOC 59 7568 (1994)
Ph ₂ S[OC(CF ₃) ₂ Ph] ₂	JACS 93 4327 (1971); 94 5003 (1972); 107 4964 (1985); 115 354, 4497 (1993) JOC 49 2682 (1984); 51 3098 (1986); 57 3347 (1992)
MeO ₂ CN ⁻ SO ₂ ⁺ NEt ₃	JACS 92 5224 (1970); 106 1518 (1984); 107 1421 (1985); 108 2343, 3731 (1986); 112 5583, 9272, 9284 (1990); 115 354, 433 (1993) JOC 35 2594 (1970); 38 26 (1973); 39 2124 (1974); 52 3614 (1987); 53 3912 (1988) TL 28 31, 4965, 5643 (1987)
<i>p</i> -MeC ₆ H ₅ OCSCl / Δ	See page 296, Section 46.
thianthrene perchlorate, 2,6-di- <i>t</i> -butyl-4-methylpyridine	TL 33 6583 (1992)
() ₂ CS / Δ	JACS 115 11654 (1993)
EtO ₂ CN=NC ₂ H ₅ , PPh ₃	JOC 54 3515 (1989) TL 31 1731 (1990)
silica gel, microwave oven	TL 32 4871 (1991)

M

Mg, Zn

JOC 44 1221 (1979)

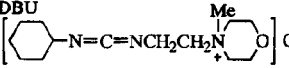
Al

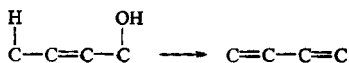
JOC 44 1221, 1340 (1979)



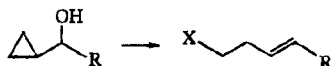
See page 287, Section 35.

XReagents

COR	(CF ₃ CO) ₂ O, Et ₃ N MsCl, Et ₃ N	Org Syn Coll Vol 8 210 (1993) SL 323 (1990)
CO ₂ R	PhCOCl, py / NH ₃ MsCl, DBU CuCl ₂ , 	JOC 60 5628 (1995) (lactone) JACS 112 6942 (1990) (lactone) JOC 52 2378 (1987) (lactone) JACS 112 6942 (1990) (lactone)
CONR ₂	SOCl ₂ , Et ₃ N / DBU	TL 34 2083 (1993)

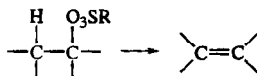


See page 466, Section 2.



<u>X</u>	<u>Reagent(s)</u>	
F	HF-py, KHF ₂ , <i>i</i> -Pr ₂ NH, PhCl	TL 28 663 (1987)
Cl	MgCl ₂ , ether, Δ	JOC 45 2566 (1980)
	MgCl ₂ , ZnCl ₂ , ether, Δ	JOC 45 2566 (1980)
	Me ₃ SiCl	TL 27 1907 (1986)
	SOCl ₂ , py	JOC 60 1435 (1995)
Br	HBr	Compt Rend 248 820 (1959)
		BSCF 1072 (1960); 1805 (1970)
		JACS 90 2882 (1968)
		Syn 37 (1979)
		JOC 50 2719 (1985)
	HBr, ZnBr ₂	JACS 90 2882 (1968)
		TL 1281 (1973)
	MgBr ₂ , ether, Δ	CC 303 (1975)
		JOC 45 2566 (1980); 59 2324 (1994)
	MgBr ₂ , ZnBr ₂ , ether, Δ	JOC 45 2566 (1980)
I	Me ₃ SiCl, LiBr	TL 27 1907 (1986)
	PBr ₃ , LiBr, collidine / ZnBr ₂	JACS 90 2882, 6225 (1968)
	HI	Syn 37 (1979)
	MgI ₂ , ether, Δ	CC 303 (1975)
		JOC 45 2566 (1980)
	MgI ₂ , ZnI ₂ , ether, Δ	JOC 45 2566 (1980)
	Me ₃ SiCl, LiI	TL 27 1907 (1986)

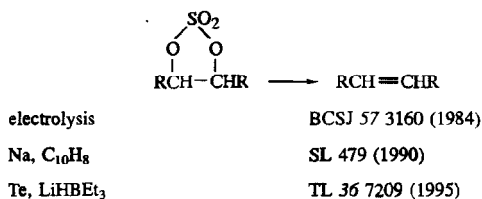
42. Sulfonate Esters



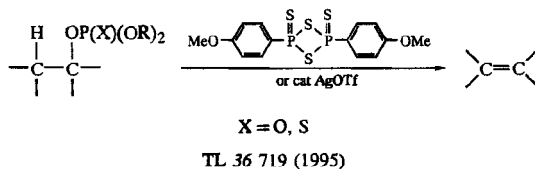
Δ (R = 2-pyridyl, 8-quinoliny)	JOC 54 389 (1989)
NaI, HMPA	JACS 109 2212 (1987)
Al ₂ O ₃	JOC 42 3173 (1977); 54 5039 (1989)
K ₂ CO ₃ , 18-crown-6	JOC 60 5319 (1995)
MOMe (M = Li, Na, K)	JOC 26 4199 (1961)
NaOC(CH ₃) ₂ CH ₂ CH ₃	JOC 56 6585 (1991)
KOR	JOC 55 5247 (1990)

KOR, 18-crown-6	JOC 55 5247 (1990)
KO- <i>t</i> -Bu	TL 28 6489 (1987)
KO- <i>t</i> -Bu, DMSO	JOC 29 742 (1964); 30 2054 (1965) Org Syn 64 50 (1985) Org Syn Coll Vol 7 117 (1990)
Et ₃ N	JOC 53 1227 (1992); 59 1027 (1994) TL 36 897 (1995)
Et ₃ N, DBU	TL 33 4041 (1992)
py	JOC 59 7568 (1994)
DBN	JOC 52 2644 (1987)
DBU	JOC 52 4044 (1987); 53 3912 (1988); 60 5319 (1995)
DMAP	TL 29 909 (1988)
DMAP, Et ₃ N	JACS 111 4120 (1989)
PhCH(Me)NMe ₂ (chiral)	TL 28 6489 (1987)
MNH ₂ (M = Li, K), NH ₃	JOC 26 4199 (1961)
KN(SiMe ₃) ₂ , 18-crown-6	JOC 60 5319 (1995)
Et ₂ NMgBr	JOC 26 4199 (1961)
<i>o</i> -NO ₂ C ₆ H ₄ SeNa / H ₂ O ₂	JOC 52 4142 (1987)

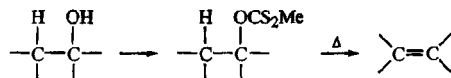
43. Sulfates



44. Phosphates and Thiophosphates



45. Xanthates

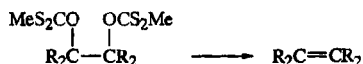


Org Rxs 12 57 (1962) (review)

TL 28 2795 (1987); 31 3409 (1990)

JACS 112 228, 1258 (1990); 113 9735 (1991); 114 2644 (1992)

JOC 59 1771 (1994)

 $(\text{R}_3\text{NH})\text{H}_2\text{PO}_2$

TL 33 5709 (1992)

JOC 58 6838 (1993)

 Ph_2SiH_2

TL 32 2569 (1991)

 $\text{Et}_3\text{SiH}, (\text{PhCO}_2)_2$

TL 32 7187 (1991)

 $n\text{-Bu}_3\text{SnH}$

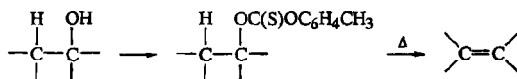
JOC 54 2217 (1989)

polymer-SnR₂H

SL 801 (1992)

46. Thiocarbonates

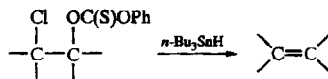
See also page 297, Section 49.



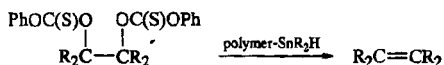
CC 1215 (1972)

JOC 45 3149 (1980); 53 1969 (1988); 59 1199 (1994)

JACS 105 7352 (1983); 108 800 (1986)

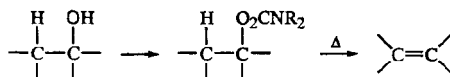


TL 35 3477 (1994)

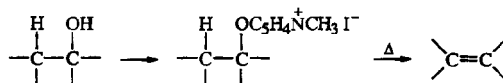


SL 801 (1992)

47. Carbamates

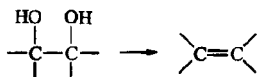


JOC 34 3604 (1969); 46 2804 (1981)

48. *N*-Methyl-4-alkoxypyridinium Iodides

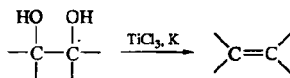
Can J Chem 50 1181 (1972)

49. 1,2-Diols and Derivatives



Review: Org Rxs 30 457 (1984)

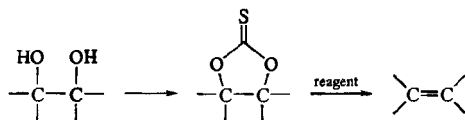
49.1. Stereospecific Cis Elimination



JOC 43 3255 (1978)

TL 28 4965 (1987)

JACS 110 5479, 5490 (1988)

P(OR)₃, Δ

JACS 85 2677 (1963); 87 934 (1965); 93 4516 (1971); 94 8627 (1972); 111 1396 (1989)

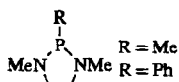
Carbohydr Res 1 214 (1965); 1 444 (1966)

TL 4645 (1967); 3655 (1978); 853 (1972)

JOC 35 3558 (1970); 54 2217, 4780 (1989); 57 1065, 5851 (1992)

Can J Chem 48 383 (1970)

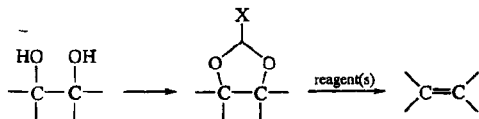
Compt Rend C 275 459 (1972)



TL 34 4121 (1993)
 TL 23 1979 (1982); 34 4121, 4357 (1993); 35
 1589 (1994)
 IACS 108 512 (1986); 110 5479 (1988)
 JOC 54 2217 (1989); 57 3473 (1992)
 TL 36 7209 (1995)
 JACS 105 1988 (1983)
 TL 2667 (1973)

Te, LiHBEt₃

Raney Ni

Ni(COD)₂

X
 Ph

Reagent(s)

RLi

CC 1593 (1968)
 Tetr 26 4339 (1970)
 JCS C 886 (1971)
 JCS Perkin I 2332 (1973)
 JOC 45 261 (1980)
 TL 30 1205 (1989)
 SL 209 (1990)
 JOC 59 1351 (1994)

LDA, KO-*t*-Bu

OR

Δ

TL 22 1471 (1981)
 Tetr 38 2395 (1982)
 JCS Perkin I 2279 (1986)
 IACS 109 7495 (1987)
 Austral J Chem 17 1392 (1964); 21 2013
 (1968)
 Carbohydr Res 7 161 (1968)
 IACS 108 1265 (1986); 114 4453 (1992)
 JOC 51 2332 (1986); 56 282 (1991)
 TL 35 8935 (1994)
 CL 879 (1986)
 JOC 53 5170 (1988); 54 4780 (1989)
 JOC 53 4780 (1988)

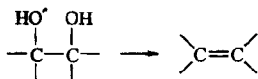
H⁺Ac₂O1,2,4-benzenetricarboxylic
 anhydrideNR₂

MeI

Ac₂O

TL 737 (1978)
 Rec Trav Chim 104 266 (1985)
 TL 5223 (1970); 27 2575 (1986)
 IACS 96 5254 (1974)

49.2. Nonstereospecific or Unknown Stereochemistry



NaOH or NaH/CS₂/MeI/*n*-Bu₃SnHCC 866 (1977)
Chem Pharm Bull 26 1786 (1978)
JCS Perkin I 2378 (1979)PBr₃/CuBr, Zn

BCSJ 52 1752 (1979)

Ph₂PCl, I₂, imidazole

JOC 55 4273 (1990)

Ph₃P, I₂, imidazoleSyn 469 (1979)
Ber 114 1809 (1981)
JOC 49 1769 (1984); 59 7267 (1994)
J Carbohydr Chem 3 189 (1984)
Carbohydr Res 205 410 (1990)
TL 36 2121 (1995)Ph₃P, triiodoimidazole, (imidazole)Syn 813 (1979)
JOC 47 4796 (1982)
J Carbohydr Chem 3 189 (1984)Ph₃P, Zn, triiodoimidazole, imidazole

IACS 111 1396 (1989)

Cl₂POX (X = OEt, NMe₂)/Li-NH₃ or Ti-THF

JOC 42 1311 (1977)

Me₃SiCl, NaI

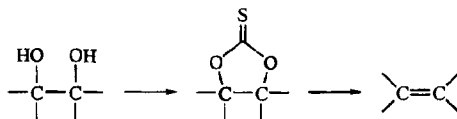
TL 23 1365 (1982)

TiCl₄, Zn, py

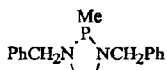
JACS 110 900 (1988)

2 MeLi/K₂WCl₆

CC 370 (1972)

MeI or *i*-PrI/(Zn)

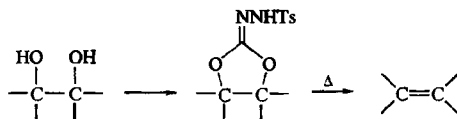
JOC 39 3641 (1974)



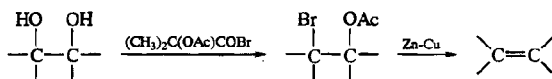
JOC 39 3641 (1974)

Fe(CO)₅

TL 4435 (1972)



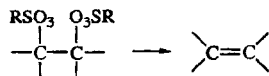
TL 3161 (1973)



JOC 54 4780 (1989)

For other methods to eliminate β -halo esters, see page 267, Section 8.

50. 1,2-Disulfonates



Na(Hg)

JACS 115 3816 (1993)

Na naphthalenide

TL 3447 (1972)

JACS 109 5524 (1987); 115 3816 (1993)

NaI, Zn

Carbohydr Res 1 338 (1965); 2 349 (1966)

BSCF 2099 (1968)

BCSJ 45 3619 (1972)

JCS Perkin I 1981 (1977)

TL 28 2183 (1987); 34 8407 (1993)

JACS 109 6403 (1987)

NaI, Zn, microwave irradiation

TL 34 8407 (1993)

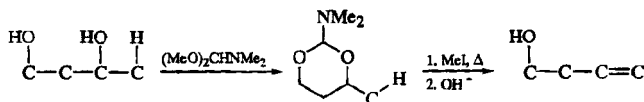
KI, Zn

Can J Chem 47 393 (1969)

KSC(S)OEt

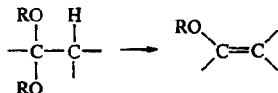
Carbohydr Res 2 349 (1966)

51. 1,3-Diols



CC 1756 (1987)

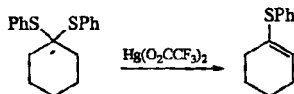
52. Acetals



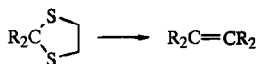
See page 931, Section 1.

53. Dithioacetals

See also page 304, Section 54.4.



JACS 105 5075 (1983)

Mo(CO)₆

JOMC 307 C49 (1986)

JOC 60 7380 (1995) (intramolecular)

W(CO)₆

CC 981 (1987)

TL 29 5131 (1988) (intramolecular)

JOC 54 263 (1989) (intramolecular); 55 1874, 1881 (1990); 60 7380 (1995) (intramolecular)

54. Aldehydes and Ketones

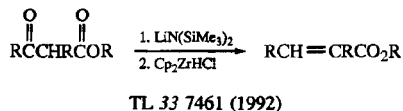
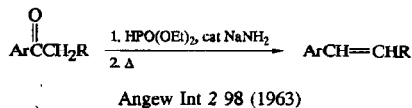
Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 4.6, p 923

54.1. Direct Elimination

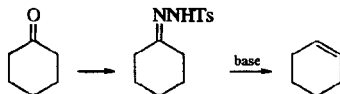


CC 935 (1973)

JCS Perkin I 809 (1975)



54.2. Arenesulfonylhydrazone Eliminations



Bamford-Stevens reaction

Review: Org Rxn 23 405 (1976)

JCS 4735 (1952)

Tetr 12 168 (1961); 31 1035 (1975)

TL 1847 (1965); 345 (1968), 2947 (1976); 29 1493 (1988); 34 2891 (1993)

Ann 691 41 (1966)

JACS 89 5734, 5736, 7112 (1967); 90 4762 (1968); 106 6006 (1984); 107 3971, 7352, 7724 (1985); 110 5112, 8483 (1988); 112 9436 (1990); 114 980, 2567 (1992); 115 6078 (1993)

Syn 595 (1970)

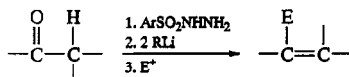
Austral J Chem 23 857 (1970)

JOC 43 147, 1404 (1978); 44 3976 (1979); 50 5460 (1985); 52 3346 (1987); 53 3912 (1988); 54 171 (1989); 55 1589 (1990); 56 1434 (1991)

Chem Pharm Bull 28 984 (1980)

Org Syn Coll Vol 6 172 (1988)

SL 22 (1992); 711 (1994)



Shapiro reaction

E⁺ = H₂O, D₂O, RX, epoxide, oxetane, DMF, CH₂O, RCHO, R₂CO, CO₂, Br₂, NCB₂, BrCF₂CF₂Br, I₂, Me₃SiCl, *n*-Bu₃SnCl

Reviews:

Org Rxs 23 405 (1976); 39 1 (1990)

Acct Chem Res 16 55 (1983)

JACS 89 5734 (1967); 90 4762 (1968); 106 3539 (1984); 107 256, 1293, 3971, 4964 (1985); 108 4586 (1986); 109 3174, 5731, 7838 (1987); 110 497, 879, 1901 (1988); 112 8126 (1990); 113 2686 (1991); 114 974, 2635, 5018 (1992); 117 634, 645 (1995)

TL 1811, 1815 (1975); 2287 (1976); 21 945, 3849 (1980); 23 3733 (1982); 27 2761, 5467 (1986); 28 1985, 4629, 6159 (1987); 34 4273 (1993); 36 5479 (1995)

Syn 801 (1976); 44 (1979)

JOC 43 147, 1404, 1409 (1978); 46 1315 (1981); 50 2438 (1985); 52 569, 2644, 3541 (1987); 53 3912, 4141 (1988); 55 1589 (1990); 56 1951, 4499 (1991); 57 2523 (1992); 58 4989 (1993)

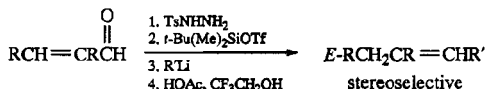
CC 65, 1121 (1981)

JCS Perkin I 2848 (1981)

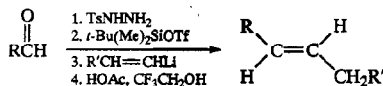
Tetr 37 3935 (1981)

Org Syn Coll Vol 7 77 (1990)

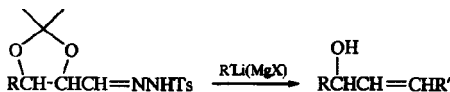
SL 465 (1991); 22 (1992)



JACS 112 8208 (1990)

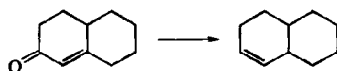


JACS 112 8208 (1990)



TL 36 5071 (1995)

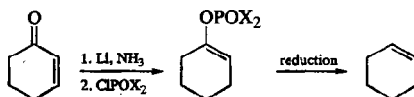
54.3. Enone Conversions

 $\text{BH}_3 / \text{Ac}_2\text{O}$

Tetr 20 957 (1964)

 Zn , HOAc, ultrasound

TL 34 357 (1993)

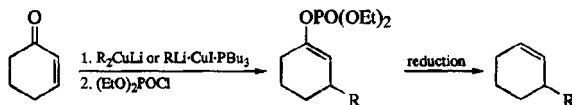
 $\text{X} = \text{OEt}, \text{NMe}_2$

TL 2145 (1969)

JACS 94 5098 (1972)

JOC 43 2715 (1978)

For methods of reduction, see page 304, Section 54.4.



TL 2145 (1969)

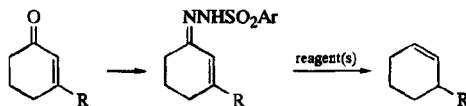
Org Syn 52 109 (1972)

JOC 43 2715 (1978)

JACS 104 1907 (1982); 106 3353 (1984); 108 5650 (1986)

Org Syn Coll Vol 6 762 (1988)

For methods of reduction, see page 304, Section 54.4.

Reagent(s) $\text{CB} / \text{NaOAc} \cdot 3\text{H}_2\text{O}$

JOC 41 574 (1976); 54 1468 (1989); 57 4590 (1992)

Org Syn 59 42 (1980)

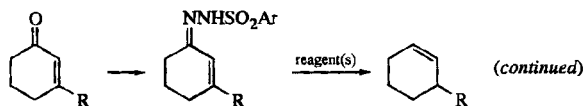
JACS 108 6276, 7686 (1986); 110 1901 (1988)

Org Syn Coll Vol 6 293 (1988)

TL 33 5009 (1992)

 NaBH_4 , HOAc

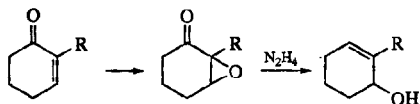
JOC 43 2299 (1978); 60 7567 (1995)

Reagent(s)NaBH₃CN

JACS 95 3662 (1973); 98 2275 (1976); 106 3353 (1984)

JOC 40 923 (1975); 50 2798 (1985)

Org Prep Proc Int 11 201 (1979) (review)



JOC 26 3615, 4781 (1961); 27 2205 (1962); 48 1217 (1983); 55 5854 (1990); 56 2076 (1991); 58 7728 (1993)
 JACS 86 269 (1964); 102 862 (1980); 106 4558 (1984); 112 2003 (1990)
 TL 28 2099 (1987)
 CC 271 (1989)

54.4. Reduction of Carbonyl Derivatives**Enamine**BH₃

TL 2039 (1964)

BH₃·SMe₂

JACS 111 384 (1989)

JOC 56 1543, 5691 (1991)

9-BBN

JACS 111 384 (1989)

JOC 56 1543, 5691 (1991)

LiAlH₄, AlCl₃

Proc Chem Soc 19 (1963)

Tetr 24 4489 (1968)

Enol ether*i*-Bu₂AlH

JOC 31 329 (1966)

Enol acetateBH₃

Gazz Chim Ital 92 309 (1962)

Enol silaneBH₃/HCl (cyclic only)

TL 4005 (1975)

Enol triflateHCO₂H, cat Pd(OAc)₂(PPh₃)₂, *n*-Bu₃N

TL 25 4821 (1984); 34 6021 (1993)

JACS 111 278 (1989); 115 49 (1993)

Org Syn Coll Vol 8 126 (1993)

JOC 60 711, 794, 4602 (1995)

Et₃SiH, cat Pd(PPh₃)₄, LiCl

JACS 108 3033 (1986)

Me₃Si(OSiHMe)_nOSiMe₃, cat Pd(PPh₃)₄, LiCl

JACS 108 3033 (1986)

$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{PPh}_3)_4$, LiCl	JACS 106 4630 (1984); 108 3033 (1986) JOC 56 3197 (1991); 60 5048 (1995)
$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{DBA})_2$, cat $(\text{C}_5\text{H}_5)_3\text{P}$, ZnCl_2	TL 29 6043 (1988) JOC 55 5833 (1990)
Enol phosphate	
Li , NH_3	JOC 54 4729 (1989); 57 4590 (1992); 60 1856 (1995)
Li , NH_3 , $t\text{-BuOH}$	CC 112 (1969) JACS 106 3353, 5025 (1984)
Li , MeNH_2 , $t\text{-BuOH}$	Helv 66 522 (1983) JACS 108 3435 (1986) JOC 57 3627 (1992)
Li , EtNH_2 , $t\text{-BuOH}$	TL 2145 (1969) Org Syn 52 109 (1972) JACS 104 1907 (1982); 106 721 (1984); 107 1308 (1985); 108 5650 (1986); 111 6287 (1989) JOC 50 2668 (1985); 57 3627 (1992); 60 1856 (1995)
Li , EtNH_2 , EtOH	JOC 59 885 (1994)
K , $\text{TiCl}_3/\text{EtOH}$	JOC 43 2715 (1978)
Enol N,N,N',N'-tetramethylphosphorodiamidates	
Li , NH_3	JACS 94 5098 (1972)
Li , NH_3 , $t\text{-BuOH}$	JOC 55 81 (1990) Org Syn Coll Vol 7 66 (1990)
Li , EtNH_2	TL 28 31 (1987)
Li , EtNH_2 , $t\text{-BuOH}$	JACS 94 5098 (1972); 112 9284 (1990)
α-Halocarbonyl compounds	
LiAlH_4/Zn , HOAc	JCS 1370 (1955)
N_2H_4	JOC 29 958 (1964)
Dithioketal	
Raney Ni	JOC 28 1443 (1963) Tetr 25 2823 (1969)

54.5. Dimerization of Aldehydes and Ketones

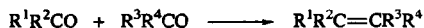


Reviews:

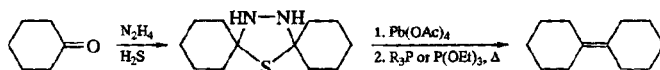
- Org Prep Proc Int 12 361 (1980)
JOC 47 248 (1982)
Acet Chem Res 16 405 (1983) (Ti reagents)
Chem Rev 88 733 (1988); 89 1513 (1989)

- Mg, cat MgI_2 TL 36 5163 (1995) (R = ferrocenyl)
- Ti-graphite JOMC 280 307 (1985)
- TiCl_3 , Li JOC 43 3255 (1978); 51 5446 (1986); 56 1940 (1991); 58 5866 (1993)
Syn Commun 11 895 (1981)
Org Syn 60 113 (1981)
JACS 106 723, 6006 (1984) (both intramolecular)
Org Syn Coll Vol 7 1 (1990)
SL 992 (1992)
- TiCl_3 , Li, ultrasound JOC 56 1940 (1991)
- TiCl_3 , Na TL 35 8561 (1994)
- TiCl_3 , Na-Hg JOC 56 6447 (1991) (intramolecular)
- TiCl_3 , K JOC 41 896 (1976) (inter- and intramolecular); 43 3255 (1978); 51 2969 (1986); 52 2905 (1987) (intramolecular)
TL 28 4965 (1987) (intramolecular)
- TiCl_3 , C_8K JACS 110 6914 (1988); 112 3018 (1990) (intramolecular)
JOC 56 6447 (1991) (intramolecular)
- TiCl_3 , Mg BSCF 2147 (1973)
- TiCl_3 , Zn-Cu JOC 42 2655 (1977); 43 3255 (1978) (intramolecular); 46 4293 (1981); 55 3075 (1990) (intramolecular)
TL 23 1777, 2723 (1982); 28 3091, 3209 (1987); 29 4369 (1988); 31 2393 (1990); 34 2175 (1993) (all intramolecular)
JACS 106 5018 (1984); 108 515, 2932, 3513 (intramolecular) (1986); 52 4885 (1987) (intramolecular); 112 1791 (1990) (intramolecular)
- $\text{TiCl}_3(\text{DME})_{1.5}$, Zn-Cu JOC 54 3748 (1989) (inter- and intramolecular); 56 4407, 6447 (intramolecular) (1991); 57 3615 (1992) (intramolecular)
JACS 113 5883 (1991) (diene); 115 7926 (diene), 10167 (1993); 117 3057 (1995) (all intramolecular)
TL 35 2609 (1994)
- TiCl_3 , Zn-Ag JOC 47 5229 (1982)
JACS 108 1239 (1986) (intramolecular)
- TiCl_3 , LiAlH_4 JACS 96 4708 (1974)
Acct Chem Res 7 281 (1974)
TL 3265 (1976); 22 3965 (1981) (enones); 33 2825 (1992)
JOC 43 3609 (1978); 52 5636 (1987); 53 5963 (1988); 57 4074 (1992) (intramolecular); 58 7149 (1993) (intramolecular); 59 878 (1994) (intramolecular)

	Ber 115 1234 (1982)
	Rec Trav Chim 101 112 (1982)
	JCS Perkin II 77 (1982)
TiCl ₄ , Na-C ₁₀ H ₈	JOC 56 6447 (1991) (intramolecular)
TiCl ₄ , Na-Hg	JOC 56 6447 (1991) (intramolecular)
TiCl ₄ , Na-K	JOC 56 6447 (1991) (intramolecular)
TiCl ₄ , Mg	TL 22 3965 (1981) (enones)
	JOC 54 877 (1989) (enones)
TiCl ₄ , Zn	CL 1041 (1973)
	Ber 117 2300 (1984)
	JACS 106 7514 (1984) (intramolecular); 108 3460 (1986); 111 6311 (1989)
	TL 26 1981 (1985) (intramolecular); 29 4377 (1988); 34 1879 (1993)
	CC 1072 (1987) (intramolecular)
	JOC 55 247 (1990); 59 3077 (1994) (intramolecular)
TiCl ₄ , Zn, py	Syn 553 (1977)
	Ber 115 3697 (1982)
	JACS 110 900 (1988); 113 4288, 4558 (1991) (both polyenes); 114 6037 (1992) (polyenes)
	JOC 59 8071 (1994)
TiCl ₄ , LiAlH ₄	JACS 96 4708 (1974)
TiCl ₄ , LiAlH ₄ , amine	CL 1127 (1976)
NbCl ₅ , NaAlH ₄	CL 158 (1982)
Mo(CO) ₆ or W(CO) ₆ or WCl ₆ , LiAlH ₄	JOC 43 2477 (1978)
WCl ₆ , 2 <i>n</i> -BuLi	JACS 94 6538 (1972)
W ₂ (OCH ₂ - <i>t</i> -Bu) ₆ py ₂	JACS 111 2324 (1989)
Zn	TL 33 4299 (1992) (2,5-cyclohexadienones)
Zn, Me ₃ SiCl	CC 1803 (1986)
Zn, ClSiMe ₂ CH ₂ CH ₂ SiClMe ₂	TL 33 3899 (1992) (ArCHO, enone)



TiCl ₃ , Li	JOC 41 3929 (1976); 43 3255 (1978); 58 4155 (1993)
	TL 23 3227 (1982)
TiCl ₃ , Zn-Cu	TL 23 3227 (1982)
W ₂ (OCH ₂ - <i>t</i> -Bu)(O)(CMe ₂)py	JACS 111 2324 (1989)



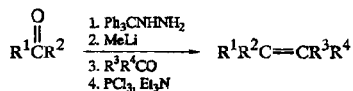
CC 1226 (1970)

JCS Perkin I 305 (1972)

JOC 38 3061 (1973); 58 43 (1993); 60 4375 (1995)

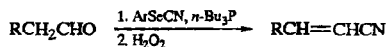
JACS 106 5018, 8174 (1984); 108 515, 2932 (1986)

See also page 271, Section 17.

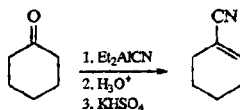


CC 22 (1984)

54.6. Miscellaneous Reactions



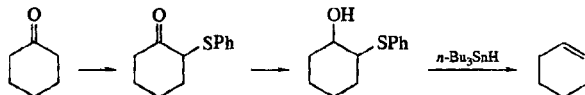
JACS 99 5210 (1977)



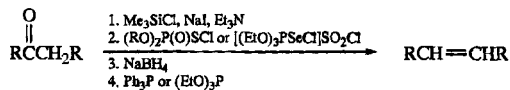
TL 1913 (1966)

JACS 94 4654 (1972)

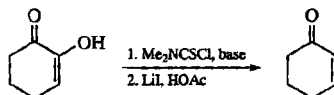
Org Syn Coll Vol 6 307 (1988)



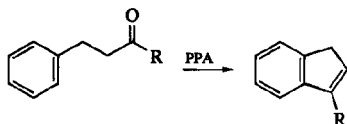
TL 4223 (1977)



TL 32 4385 (1991)



JOC 53 1110 (1988)

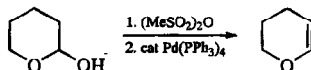


J Med Chem 31 1316, 1754 (1988)

J Phys Chem 92 6249 (1988)

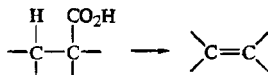
IOC 54 1485 (1989)

55. Lactols



JACS 114 1491 (1992)

56. Carboxylic Acids



$\text{PhI}(\text{OAc})_2$, $\text{Cu}(\text{OAc})_2$

IOC 51 402 (1986)

$\text{Pb}(\text{OAc})_4$

JACS 83 927 (1961)

$\text{Pb}(\text{OAc})_4$, cat $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, py

JACS 87 1811, 3609 (1965); 107 2149 (1985);
108 4603 (1986); 112 363 (1990); 113 1386
(1991)

IOC 32 2045 (1967); 39 2217 (1974); 55 1965
(1990)

TL 405, 5173 (1968); 399 (1974); 26 6397 (1985)

Tetr 24 2215 (1968)

JCS C 1047 (1969)

Org Rxs 19 279 (1972) (review)

Syn 541 (1973); 889 (1974)

$\text{Pb}(\text{OAc})_4$, $\text{Cu}(\text{OAc})_2$, cat py

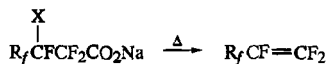
IOC 55 1965 (1990)

cat $(\text{Me}_2\text{PPh})_2\text{Rh}(\text{CO})\text{Cl}$, Ac_2O

IOC 58 18 (1993)

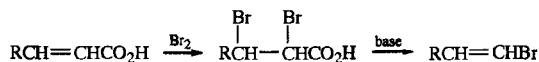
cat $\text{PdCl}_2(\text{PPh}_3)_2$, Ac_2O

IOC 58 18 (1993)

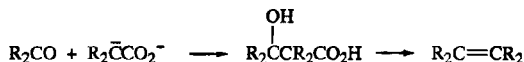


$\text{X} = \text{F}, \text{Cl}$

IOC 60 89 (1995)



See page 741, Section 12.



Syn elimination

MsCl, Na₂CO₃/Δ

TL 4569 (1968)

JCS Perkin I 884 (1976)

ArSO₂Cl, py/Δ

JACS 94 2000 (1972)

Can J Chem 51 981 (1973) (vinyl ethers)

JOC 39 1322, 1650 (1974); 43 4574 (1978) (vinyl ethers); 44 356 (1979); 46 3359 (1981); 52 3143 (1987); 60 5378 (1995)

CC 52 (1979) (alkenes, vinyl ethers); 1199 (1986) (allylic silanes)

Syn 388 (1979) (vinyl ethers)

Helv 62 2825 (1979)

TL 28 2753, 3103, 5921 (allylic silane) (1987); 33 2465 (1992); 36 7643 (1995)

Anti elimination

EtO₂CN=NCO₂Et, PPh₃

Angew Int 16 255 (1977); 22 628 (1983)

CC 52 (1979) (alkenes and vinyl ethers)

JOC 54 2311 (1989)

(CH₃O)₂CHN(CH₃)₂, Δ

TL 1545 (1975); 2953 (1978) (dienes); 1909 (1979) (mechanism); 27 5417 (1986); 33 2465 (1992)

Helv 62 2825 (1979)

Ber 115 3453 (1982) (dienes)

CC 1199 (1986) (allylic silanes)

JOC 58 3602 (1993)

(Me₃CCH₂)₂OCHNMe₂, Δ

JOC 48 5341 (1983); 53 1584 (1988); 60 6375 (1995)

Nonstereospecific

VOCl₃, (proton sponge)

JACS 111 3069 (1989)

cat WOCl₄, proton sponge

TL 33 6783 (1992)

Unknown stereochemistry or no stereoselectivity

Δ

TL 23 5271 (1982)

VOCl₃

JOC 55 5619 (1990)

p-MeC₆H₄N=VCl₃

JOC 55 5619 (1990)

For other examples of β-lactone thermolysis to alkenes, see:

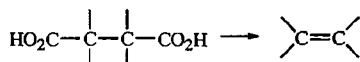
JOC 31 4043 (1966); 54 573 (1989) (theory); 56 1176 (1991); 60 578, 3879 (1995)

JACS 90 2333 (1968)

Angew Int 14 765 (1975)



JACS 102 2841 (1980)



Review: Tetr 40 2585 (1984)

electrolysis

JACS 85 165 (1963); 89 3922 (1967)

Ber 100 2427 (1967)

TL 5117, 5123 (1968)

PbO₂

JACS 74 4370 (1952)

Pb(OAc)₄, py

Helv 41 1191 (1958)

Angew 70 343 (1958)

JACS 83 1705 (1961); 85 165 (1963); 90 113 (1968);
98 628 (1976)JOC 30 1431 (1965); 42 1654 (1977); 53 1722
(1988)

CC 214 (1965); 899 (1974); 1038 (1979)

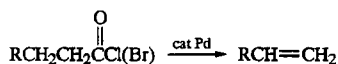
Ber 100 2427 (1967)

Org Rxs 19 279 (1972) (review)

Cu₂O, quinoline, bipy

TL 4447 (1976)

JACS 109 4626 (1987)

57. Acid Halides

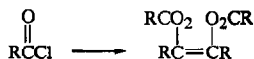
JACS 90 94 (1968)

Syn 157 (1969)

Tetr 30 11 (1974)

JOC 41 3452 (1976)

TL 27 4615 (1986)



Li(Hg)

Ber 116 1603 (1983)

Na(Hg)

Ann 135 172 (1865); 155 104 (1870)

Ber 16 995 (1883); 24 1264 (1891)

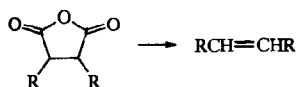
R₃SnSnR₃Yakugaku Zasshi 90 59 (1970) [CA 72 90593j
(1970)]

Ni

JOC 53 2381 (1988)

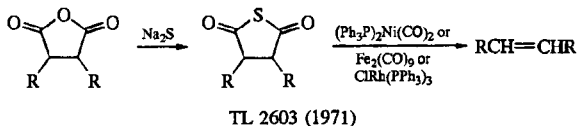
Ni(CO) ₄	TL 1841 (1963)
Fe(CO) ₅	JOMC 248 221 (1983)
Cu	JOC 53 2381 (1988)
1,2:5,6-dibenzocyclooctatetraene dianion	JOC 44 4477 (1979)
electrolysis	JOC 47 142 (1982); 57 786 (1992) Syn Commun 13 327 (1983)

58. Acid Anhydrides



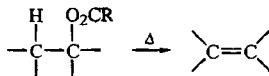
Review: Tetr 40 2585 (1984)

PbO ₂	JACS 74 4370 (1952) Ann 585 154 (1954) JOC 23 141 (1958) Org Rxs 19 279 (1972) (review)
Pb(OAc) ₄ , py	Helv 41 1191 (1958) JACS 83 1705 (1961); 85 3297 (1963); 90 113 (1968); 93 6092 (1971) Org Rxs 19 279 (1972) (review)
Ni(CO) ₂ (PPh ₃) ₂	TL 2603 (1971) JOC 41 887 (1976)
Cu ₂ O, bipy, quinoline, H ₂ O	JACS 109 4626 (1987) JOC 59 661 (1994)
electrolysis	JOC 53 3908, 5168 (1988)



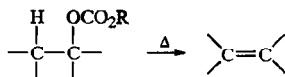
59. Esters and Lactones

See page 309, Section 56, for elimination of β -hydroxy acids via β -lactones.



Chem Rev 60 431 (1960) (review)
Org Syn Coll Vol 4 746 (1963)

JOC 52 5034 (1987); 59 845, 3775, 5128 (1994); 60 191 (1995)
 TL 28 1519 (1987); 31 5617 (1990)



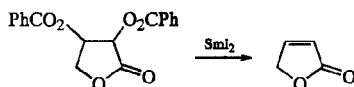
R

Me

JOC 57 50 (1992)

Ph

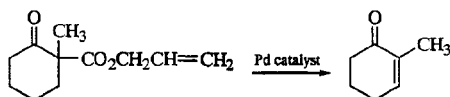
SL 972 (1994)



TL 33 573 (1992)



TL 22 1441 (1981)

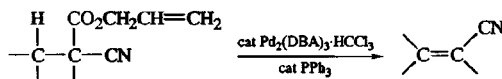


JACS 104 5844 (1982)

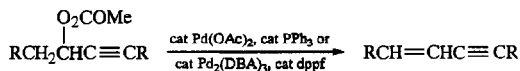
TL 24 1797 (1983); 30 4999 (1989); 32 1433 (1991)

CL 1133 (1984)

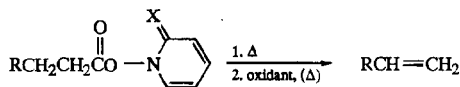
Syn 1009 (1984)



CC 118 (1986)



TL 34 7615 (1993)



X

Oxidant

S

m-ClC₆H₄CO₂H

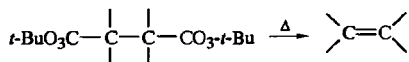
Tetr 43 4297 (1987)

TL 30 7111 (1989)

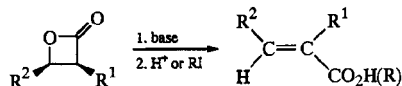
Se

O₃

Tetr 41 4347 (1985)

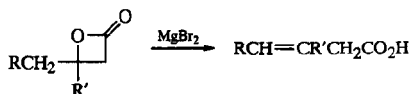


CC 98 (1969)

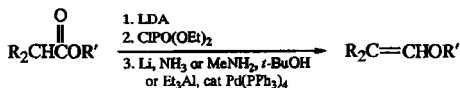


JACS 102 3620 (1980)

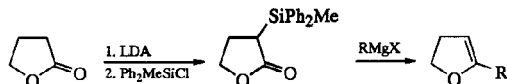
JOC 57 389 (1992); 58 4219 (1993)



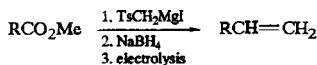
TL 30 531 (1989)



JOC 52 2303 (1987); 59 5758 (1994)



TL 23 271 (1982)



CL 69 (1978)

60. Thioesters



hv

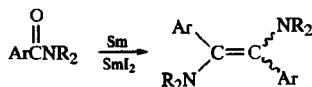
Angew Int 27 1362 (1988)

JACS 115 3558 (1993); 117 10227 (1995)

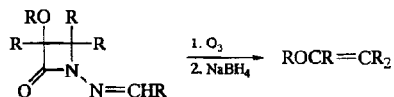
Na-C₁₀H₈/MeI/*n*-Bu₃SnH

JACS 112 3040 (1990)

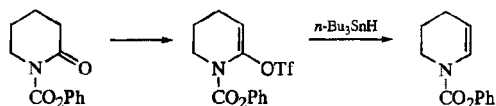
62. Amides and Lactams



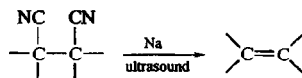
JACS 114 8729 (1992)



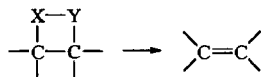
JOC 60 6012 (1995)

63. Imides

JOC 60 2656 (1995)

64. Nitriles

TL 27 4347 (1986)

65. Miscellaneous ReactionsX-Y = CR₂CR₂, CR₂O, CR₂S, CR₂C=O, OC=O, SC=O, NRC=O

Reviews:

Angew Int 21 225 (1982)

J Chem Ed 59 313 (1982)



TL 36 459 (1995)

3. ALKYLIDENATION OF CARBONYL AND RELATED COMPOUNDS

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 1.11, p 341



CH₂Br₂, Et₃NH (on RCHO)

CC 2041 (1994)

RCHO, TiCl₄

TL 31 677 (1990) (enones)

RCHO, TiCl₄, Ti(O-*i*-Pr)₄

TL 31 677 (1990) (enones)

RCHO, cat Cp₂ZrH₂, cat NiCl₂

JOC 52 2239 (1987)

ArCHO, NaOH

JACS 117 5235 (1995)

ArCHO, cat Ba(OH)₂·C200, sonication

TL 28 4541 (1987)

LDA/RCHO

JACS 106 3384 (1984) (enone)

TL 28 333 (1987) (enone)

LDA/H₂CO/MsCl, Et₃N

JOC 53 611 (1988)

LDA/H₂CO/TsCl, py/DBU

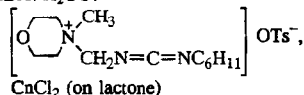
JOC 52 4647 (1987); 58 1030 (1993) (lactone)

LDA/H₂CO/MsCl, Et₃N/DBU

JOC 53 1441 (1988)

JACS 114 7387 (1992)

LDA/H₂CO/



Syn Commun 16 1593 (1986)

JOC 52 2378 (1987); 53 1616 (1988)

TL 28 5081 (1987)

LDA/CH₃COCH₃/I₂

JACS 108 4556 (1986)

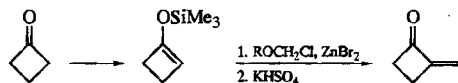
NaOMe, HCO₂Me/H₂CO, K₂CO₃

Syn 665 (1983)

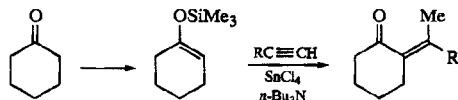
base, HCO₂R/H₂CO; py, Et₃N or K₂CO₃

JOC 32 3434 (1967)

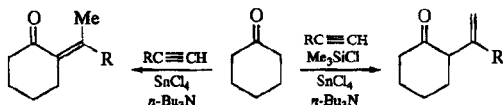
$\text{MeOCO}_2\text{MgOMe}/\text{H}_2\text{CO}$, Et_2NH or PhNHMe , NaOAc , HOAc	JOC 38 2489 (1973); 57 4567 (1992)
$\text{LiN}(\text{SiMe}_3)_2/\text{HCO}_2\text{Me}/\text{H}_2\text{CO}$, K_2CO_3	JACS 105 2435 (1983) JOC 50 3957 (1985)
H_2CO , $(\text{R}_2\text{N}^+\text{H}_2)\text{Cl}^-$ $(\text{CH}_2\text{O})_3$, PhNHMe , $\text{CF}_3\text{CO}_2\text{H}$	JACS 95 4873 (1973) TL 2111, 2955 (1978) Org Syn 60 88 (1981) Syn 952 (1983) JACS 111 3728 (1989) Org Syn Coll Vol 7 332 (1990)
$\text{LDA}/(\text{Me}_2\text{N}^+=\text{CH}_2)\text{I}^-/\text{MeI}/\text{base}$	JACS 98 6715 (1976) (lactone); 99 944 (1977); 116 495 (1994) TL 1621 (1977); 31 2393 (1990) (lactone) JOC 44 1391 (1979); 45 524 (1980)
$\text{CF}_3\text{CO}_2\text{CH}(\text{CF}_3)\text{NR}_2$ ($\text{CR}_2 = \text{CHCF}_3$)	TL 34 5711 (1993)
$\text{BrCH}_2\text{SO}_2\text{Br}$, $h\nu$ (on enol silane)/DBN	JOC 49 3664 (1984)
RCHISO_2Br , $h\nu$ (on enol silane)/DBN	JACS 108 4568 (1986)
$\text{LDA}/\text{PhCH}_2\text{SCH}_2\text{Br}/\text{NaIO}_4/\Delta$ (on acids and ketones)	JOC 51 2981 (1986)
LDA or Et_3N , $\text{Me}_3\text{SiCl}/\text{PhSCH}_2\text{Cl}$, TiCl_4 / NaIO_4/Δ	TL 993, 995 (1979)
$\text{LDA}/(\text{PhSe})_2/\text{LDA}/\text{RCHO}/\text{SOCl}_2$, Et_3N (on amide)	JOC 51 3108 (1986)
$\text{H}_2\text{C}=\text{C}(\text{OAc})\text{CH}_3\text{-H}^+$ or $\text{Me}_3\text{SiCl-Et}_3\text{N}/$ RCHClOMe , $\text{Zn}(\text{Cu})$, $\text{CH}_2\text{I}_2/\text{KHSO}_4$	JACS 101 984 (1979)



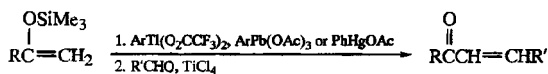
JOC 53 611 (1988)



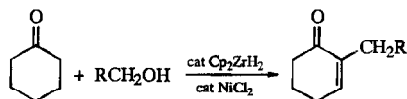
JACS 115 3362 (1993)



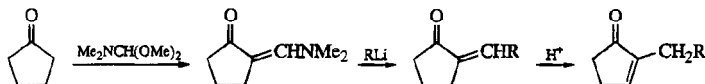
SL 51 (1995)



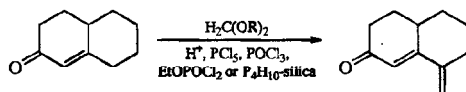
JOC 53 1022 (1988)



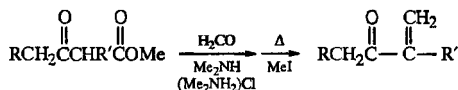
JOC 52 2239 (1987)



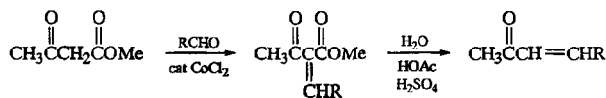
JOC 43 4248 (1978)



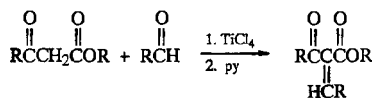
Syn 34 (1982)



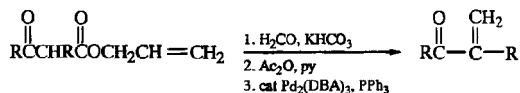
TL 5037 (1973)



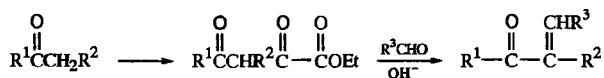
TL 32 1663 (1991)



TL 32 7731 (1991)



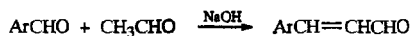
TL 27 2483 (1986)



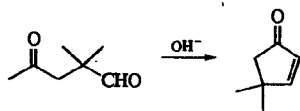
JOC 42 1180 (1977)



See page 1317, Section 8 and page 1513, Section 13 (directed aldol).



Ber 76 676 (1943)



Syn Commun 10 273 (1980)

Org Syn Coll Vol 8 208, 620 (1993)



NaOH

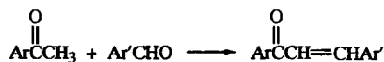
Org Syn Coll Vol 1 77 (1941)

Ber 76 676 (1943)

Syn 647 (1980)

M(OAc)₂ (M = Co, Ni, Cu, Zn), bipy

BCSJ 53 1366 (1980)



NaOH

Syn 647 (1980)

JOC 52 5560 (1987)

KOH

JOC 58 1751 (1993)

cat Ba(OH)₂·C200

TL 28 4541 (1987)

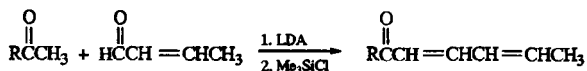
TiCl₄, Et₃N

TL 28 4135 (1987)

cat Co(II)-polymer

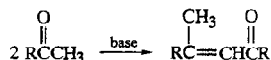
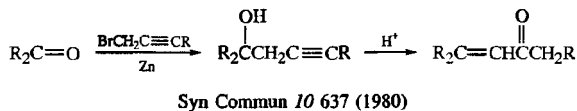
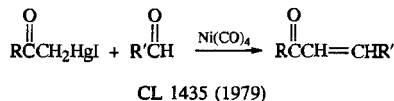
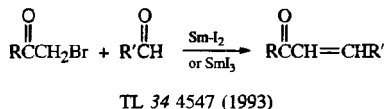
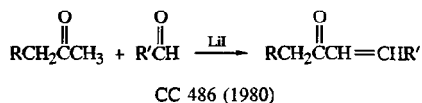
CL 1401 (1979)

BCSJ 55 3208 (1982)



R = alkyl, aryl, OR

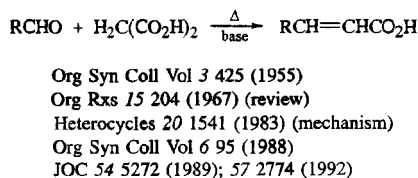
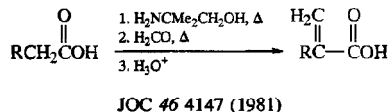
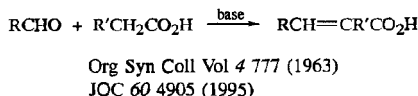
TL 32 1791 (1991)

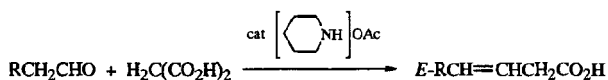


Base

$\text{Al}(\text{O}-i\text{-Bu})_3$ Org Syn Coll Vol 3 367 (1955)

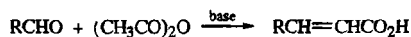
Al_2O_3 Syn 60 (1982)





ICS 740 (1931); 557 (1933)

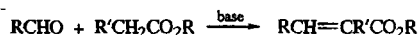
28 93 (1987)



Org Rxs 1 210 (1942) (review)

Org Syn Coll Vol 3 426 (1955)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 1.12, p 395 (review)



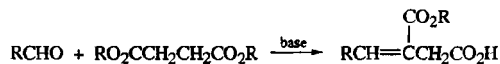
Org Syn Coll Vol 1 252 (1941)

Ber 76 676 (1943)

Org Rxs 6 1 (1951)



JOC 60 4635 (1995)

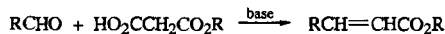


Stobbe condensation

Org Rxs 6 1 (1951) (review)

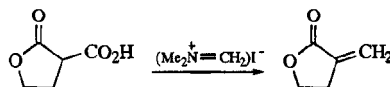
Ind J Chem B 21 658 (1982)

TL 36 3453 (1995)

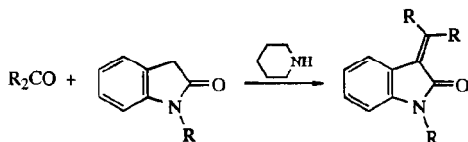


JACS 68 376 (1946)

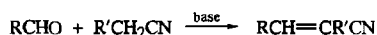
JOC 57 7248 (1992)



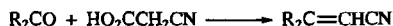
Tetr 38 2797 (1982)



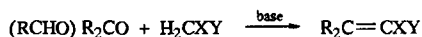
JOC 57 4765 (1992)



Org Syn Coll Vol 3 715 (1955); 7 108 (1990)
JOC 44 4640 (1979)



piperidine JOC 58 6650 (1993)
NH₄OAc, HOAc BSCF II 116 (1982)

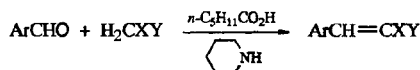


Reviews:

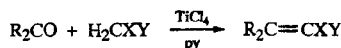
Org Rxs 15 204 (1967)
Can J Chem 45 1001 (1967); 47 3137 (1969)

<u>X</u>	<u>Y</u>	
Ar	CN	BCSJ 56 1885 (1983) JACS 111 5954 (1989) JOC 60 3750 (1995)
COR	COR	Syn 667 (1974) Syn Commun 13 1203 (1983) TL 29 2261 (1988)
	CO ₂ R	Tetr 28 663 (1972) JCS Perkin I 3132 (1981) TL 29 2261 (1988) JOC 55 319 (1990) Heterocycles 20 2393 (1983)
CO ₂ R	CN	JOC 4 493 (1939); 48 3603 (1983); 55 5793 (1990) Ber 76 676 (1943) Org Syn Coll Vol 3 377 (1955) TL 4723 (1970); 35 9399 (1994) Tetr 29 635 (1973) JCS Perkin I 3132 (1981) Heterocycles 20 1541 (1983) Org Syn 64 63 (1985)
	CO ₂ SiMe ₃	TL 35 9323 (1994)
	N ₃	JOC 60 1800 (1995)
	NO ₂	Tetr 28 663 (1972)
	PO(OR) ₂	Tetr 30 301 (1974) JOC 59 6717 (1994)
	CN	JACS 59 2327 (1937); 95 4873 (1973) JOC 22 1704 (1957); 27 3505 (1962); 29 5195 (1984) TL 23 4927 (1982); 26 4453 (1985); 29 2261 (1988); 33 7535 (1992) BSCF II 116 (1982)
CONH ₂	CN	TL 23 4927 (1982)

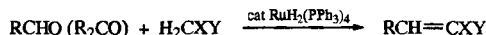
<u>X</u>	<u>Y</u>	(continued)
CN	CN	JOC 27 3505 (1962); 48 1366, 3852 (1983); 49 5195 (1984); 53 1689 (1988); 54 3800 (1989); 60 3750, 4051 (1995) Chem Rev 69 591 (1969) (review) Syn 165 (1978) (review) TL 23 4927 (1982); 26 4453 (1985); 29 2261 (1988); 33 7535 (1992); 35 9399 (1994) BCSJ 56 1885 (1983) Tetr 39 1161, 1167 (1983) TL 23 4927 (1982)
	PO(OR) ₂	
PO(OR) ₂	PO(OR) ₂	Tetr 30 301 (1974)



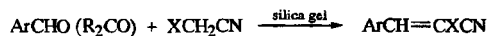
X, Y = COR, COR; CN, CO₂R; COR, CO₂R; CO₂R, CO₂R; Ph, NO₂; Ph, COR
JACS 72 4638 (1950); 117 11205 (1995)



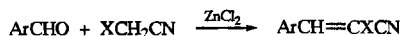
<u>X</u>	<u>Y</u>	
COR	CO ₂ R	JOC 59 5305 (1994); 60 2664 (1995)
	CN	JOC 59 5305 (1994)
CO ₂ R	CO ₂ R	TL 4723 (1970) Tetr 29 635 (1973) JOC 58 4298 (1993) JACS 117 11205 (1995) Syn Commun 473 (1980)
	CN	
CN	CN	JOC 54 3800 (1989)



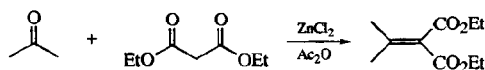
X, Y = CO₂R, CN; Ph, CN; CN, CN
JACS 111 5954 (1989); 117 12436 (1995)



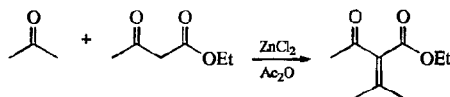
X = COR, NO₂, CN
JOC 57 1838 (1992)



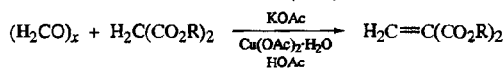
X = CO₂R, CONH₂, CN
TL 32 5821 (1991)



Org Syn Coll Vol 6 442 (1988)

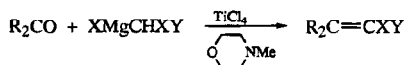


JOC 60 1195 (1995)



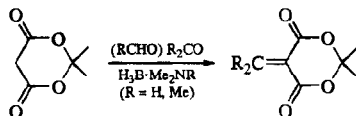
JOC 4 493 (1939)

Org Syn Coll Vol 7 142 (1990)

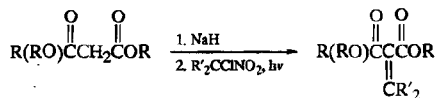


X, Y = SO₂Ph, SO₂Ph; R₂SO₂, CN

TL 35 7589 (1994)

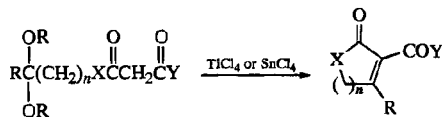


TL 24 4951 (1983)



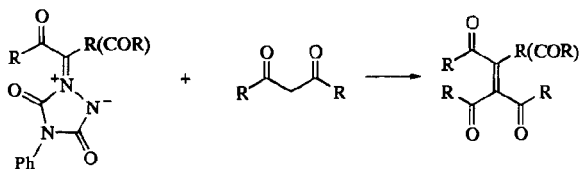
Syn 62 (1981)

TL 24 1787 (1983)



X = C, O, NR; Y = C, OR; n = 1, 2

JACS 115 8849 (1993)



JACS 113 7240 (1991)

4. WITTIG AND RELATED REACTIONS

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 1, Part 3.1, p 729

See also page 317, Section 3.

1. Wittig Reaction



1.1. General

Quart Rev 17 406 (1963) (general)

Angew Int 3 250 (1964) (unsaturated fatty acids); 16 423 (1977) (industrial practice); 21 545 (1982) (synthesis of $\text{R}^1\text{R}^2\text{C}=\text{PPh}_3$)

Pure Appl Chem 9 255 (general), 271 (stereochemistry) (1964); 51 515 (1979) (polyenes)

Org Rxs 14 270 (1965) (general); 25 73 (1977) (phosphoryl-stabilized anions)

A. W. Johnson, "Ylid Chemistry," Academic Press, New York (1966)

Topics Stereochem 5 1 (1970) (stereochemistry); 21 1 (1994) (stereochemistry and mechanism)

Syn 765 (1975) (bis-Wittig reaction)

I. Gosney, A. G. Rowley in "Organophosphorus Reagents in Organic Synthesis," Ed. J. I. G. Cadogan, Academic Press, New York (1979), Chpt 2

JCS Perkin I 1 (1979) (polymer-supported reagents)

Ann 1705, 2117 (1981) (pheromones and dienes)

Syn Commun 11 125 (1981) (phase transfer); 12 107 (phase transfer), 469 (preparation of ylid via decarboxylation) (1982)

J Chem Res (S) 142 (1981) (phase transfer); 188 (1982) (D labeling in vinylic positions)

JACS 104 5821 (1982) (stereochemistry); 106 7514 (1984) (bis-Wittig reaction); 107 1068 (stereochemistry), 6598 (bis-Wittig reaction) (1985); 111 2351 (1989) (bis-Wittig reaction); 112 1159 (1990) (bis-Wittig reaction)

Chimia 36 396 (1982) (preparation of ylid)

Russ Chem Rev 51 1 (1982) (fluorine-containing ylids)

Topics Curr Chem 109 85 (natural products), 165 (industrial applications) (1983)

Phosphorus and Sulfur 18 171 (1983) (general)

Ann 2135 (1983) (promotion by high pressure)

JOC 49 4293 (1984) (preparation of phosphonium salts); 51 3302 (1986) (concentration effects on stereochemistry); 53 3838 (1988) (stereoselectivity); 54 3695 (1989) [$\text{Ba}(\text{OH})_2$ catalyst]; 55 493

(mechanism), 3446 (enantioselective) (1990); 57 2865 (1992) (reactivity, stereoselectivity); 58 6509 (1993) (stereoselectivity); 60 156 (1995) (stereoselectivity)
 TL 28 2191, 4377 (1987) (both promotion by high pressure); 29 2531 (phase transfer, alkylidene cyclopropanes), 6823 (on lactols) (1988); 31 3529 ($\text{Ph}_3\text{P}=\text{CHCHRCHOTMS}$) (1990)
 Chem Rev 89 863 (1989) (review)

1.2. Intramolecular Wittig

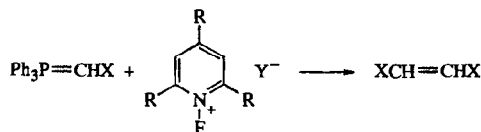
Helv 60 68, 81 (1977)
 Tetr 36 1717 (1980)
 CC 14 (1981) (indole synthesis)
 TL 23 3543 (1982) (bicycloalkenones); 29 2063 (1988) (2-alken-4-olide, 2-alkene-4-lactam); 30 7393, 7397 (1989) (both 2-alken- ω -olide)
 JOC 47 5372 (1982) (bicycloalkenes)
 Angew Int 22 780 (1983) (2-alken- ω -olide)
 Syn 419 (1989) (2-alken- ω -olide)

1.3. Mechanism

Angew Int 7 650 (1968)
 JACS 95 5778 (1973); 103 2823 (1981); 104 5821 (1982); 106 1873 (1984); 107 1068 (1985); 108 7664 (1986); 110 3940, 3948 (1988); 111 5861 (1989); 112 3905 (1990); 115 8570 (1993)
 TL 2707 (1979)
 CC 1072 (1979)
 Pure Appl Chem 52 771 (1980)
 JOC 52 4637 (1987)

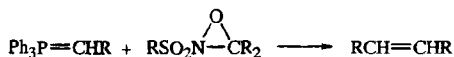
1.4. Miscellaneous Reactions

For a review of reactions of carbonyl compounds other than aldehydes or ketones, see Chem Soc Rev 17 1 (1988).

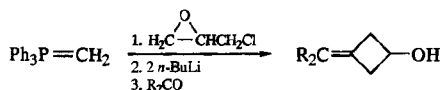


X = Ar, COR, CO₂R; R = H, Me; Y = OTf, BF₄

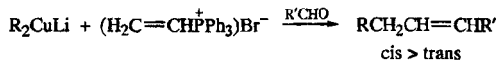
TL 35 8951 (1994)



JOC 55 360 (1990) (inter- and intramolecular)

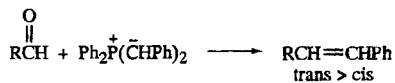


TL 36 5591 (1995)

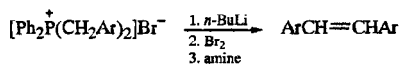


R = alkyl, aryl, vinylic

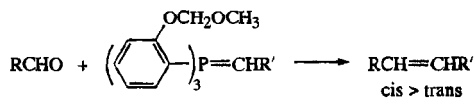
TL 26 1799 (1985)



TL 30 5263 (1989)



TL 35 5903 (1994)

 R' Me, *n*-Pr, Ph

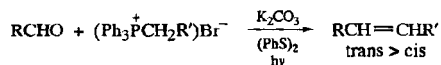
Syn 109 (1990)

Ph

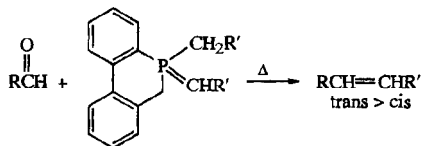
SL 605 (1990)

 CO_2R

SL 125 (1993)

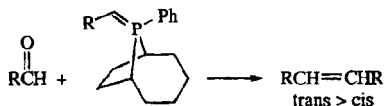


SL 817 (1994)

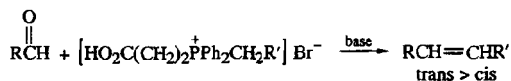


TL 28 3445 (1987)

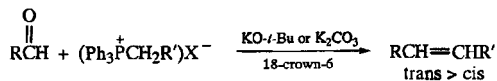
JOC 58 6509 (1993)



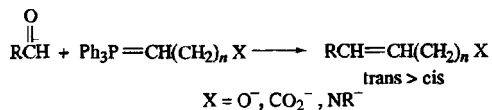
JOC 58 1985, 6509 (1993)



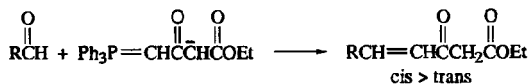
TL 28 1165 (1987)



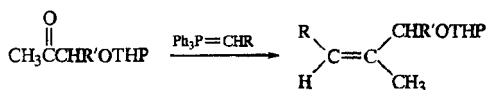
Syn 784 (1975)



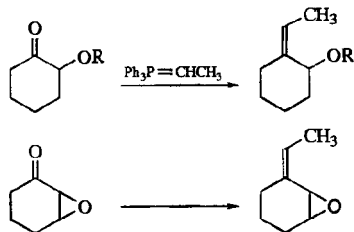
TL 22 4185 (1981); 26 311 (1985); 33 8055 (1992)
JACS 107 217 (1985)



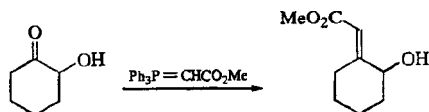
TL 27 739 (1986)



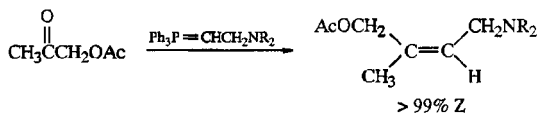
JOC 45 4260 (1980)
CL 1711 (1981)



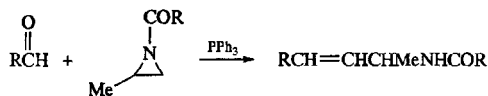
JOC 50 5910 (1985)



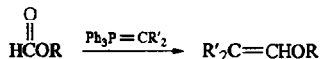
JOC 52 2629 (1987)



TL 23 2219 (1982)



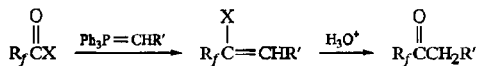
TL 31 2661 (1990)



JOC 41 1272 (1976); 49 3595 (1984)

CL 967 (1981)

TL 23 427 (1982)



X

OR

Ber 103 2011 (1970)

JOC 57 3807 (1992)

TL 35 2907 (1994)

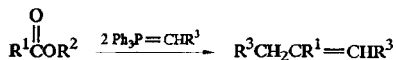
OSiMe₃

J Fluorine Chem 39 271 (1988)

NR₂

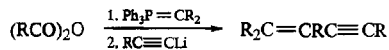
Syn 309 (1989)

JOC 57 3807 (1992)

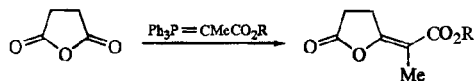


TL 1439 (1975)

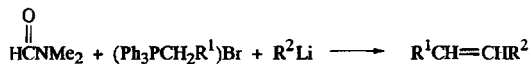
JOC 43 3306 (1978); 44 3157 (1979)



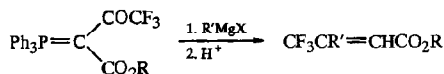
CC 703 (1987)



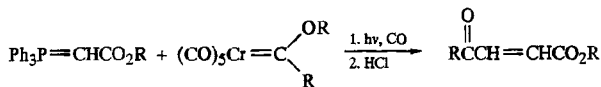
JOC 55 5217 (1990)



JOC 57 6667 (1992)



JOC 58 4564 (1993)



JACS 114 4079 (1992)

2. β -Oxido Ylids

Angew Int 5 126 (1966)

Ann 708 1 (1967)

Syn 38 (1969)

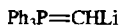
Ber 103 2814 (1970)

TL 447 (1970); 3231 (1977)

JACS 92 226, 6635, 6636, 6637 (1970); 93 4835 (1971)

JOC 45 3350 (1980); 50 3111 (1985)

3. Ylid Anions



JACS 104 4724 (1982)

TL 26 555 (1985)



Phosphorus and Sulfur 30 135 (1987)

TL 29 485 (1988); 30 5263 (1989); 35 5903 (1994)

4. Phosphonates

4.1. General

Ber 92 2499 (1959); 95 581 (1962)

JACS 83 1733 (1964); 89 5292 (1967)

TL 1821 (1971); 21 2161 (1980) (KF·2H₂O as base); 28 2951 (1987) [cat Ba(OH)₂, EtO₂CCH₂PO(OEt)₂, ultrasound]; 29 477 (α -deuteration), 1773 (chiral phosphonate), 1775 (chiral phosphonate), 2655 (2-fluoro-2-alken-1-ones) (1988); 30 675 (2-alkylidene-5-alkanolides), 3779 (2-alkenamides) (1989); 34 1479 (1993) (enamides); 35 3383, 5907 (1994); 36 6563 (1995) (3-sulfinylacrylates)

Org Syn Coll Vol 5 509 (1973)

Syn 869 (1974) (phase transfer); 884 (1979) (phase transfer); 117 (1981) (crown ether use); 300 (1983) (heterogeneous); 1097 (1985) [Ba(OH)₂, phase transfer]

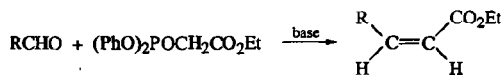
Chem Rev 74 87 (1974); 89 863 (1989) (both reviews)

Org Rxs 25 73 (1977) (review)
 JCS Perkin I 2516 (1980) (polymer-supported phosphonates)
 Syn Commun 14 701 (1980) (phase transfer)
 J Chem Res (S) 143 (1981) (phase transfer)
 Z Chem 22 117 (1982) (heteroatom-substituted olefins)
 Phosphorus and Sulfur 14 385 (1983) (reaction conditions)
 CL 1375 (1983)
 Tetr 40 5153 (1984) (stereochemistry); 41 1259 (1985) (alumina)
 JOC 50 2624 (1985) (α,β -unsaturated esters); 52 3875 (1987) (ultrasound, phase transfer); 54 1992, 3359, 3936 (inorganic bases) (1989); 55 3386 (1990) ($\text{RCH}=\text{CHCO}_2\text{R}$ stereochemistry); 58 3802 (1993) (chiral)
 CC 1509 (1987) (enone synthesis)
 SL 774, 783 (1993)

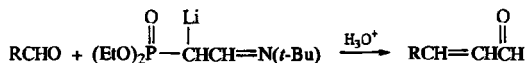
4.2. Intramolecular

JACS 90 5926 (1968) (enones); 100 7069 (1978) (2-alken- ω -olide); 103 1222 (1981); 104 2027, 2030 (1982); 106 260, 1148 (1984); 107 7967 (1985) (enone); 108 1035, 3110, 3112, 6389 (1986); 109 2208 (1987) (enone); 110 4685 (1988) (enone); 111 5792 (1989) (enone)
 Angew Int 7 300 (1968) (2-alken-4-olide); 20 286 (1981)
 CC 445 (1970) (2-alkene-4-lactam, 2-alkene-5-lactam); 413 (1986) (enone)
 JOC 44 4010, 4011 (1979) (2-alken- ω -olide); 52 1375 (1987) (enone)
 Helv 62 2661 (1979) (enones)
 TL 27 2157, 4873 (1986); 28 2717 (1987) (2-alken- ω -olide); 31 1735 (1990) (enone); 32 6947 (1991) (cyclic vinylic ethers)

4.3. Miscellaneous Reactions



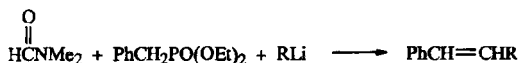
TL 36 4105 (1995)



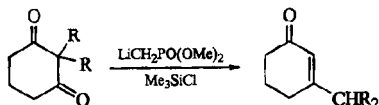
JOC 51 5111 (1986)



JOC 55 4639 (1990)

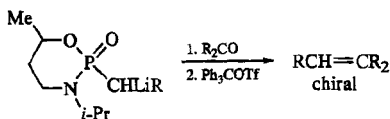


JOC 57 6667 (1992)

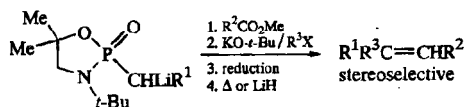


JOC 55 3971 (1990)

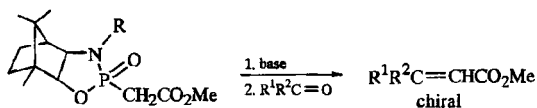
5. Phosphonamidates [(R₂N)(RO)POCHLiR]



JACS 114 10674 (1992)



JACS 115 10386 (1993)



JOC 59 6887 (1994)

6. Phosphonic Acid bis Amides [(R₂N)₂POCHLiR]

JACS 88 5652, 5653 (1966); 90 6816 (1968); 106 5754 (1984) (enantioselective); 112 5583 (1990); 117 6732 (1995) (enantioselective)

TL 32 1317 (1991); 33 7655 (1992) (enantioselective)

JOC 58 100, 4165 (1993); 59 1855 (1994) (enantioselective); 60 7192 (1995) (enantioselective)

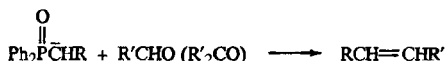
7. Phosphinothioic Amides [PhPS(NR₂)CHLiR]

JACS 104 7041 (1982)

TL 23 5005 (1982)

JOC 52 34 (1987)

8. Phosphine Oxides



Ber 92 2499 (1959)

JCS Perkin I 639 (1976) (1,3-alkadienes); 550 (1977) (1,3-alkadienes); 3099 (1979) (vinyl ethers); 2893 (1983)

B. J. Walker, "Organophosphorus Reagents in Organic Synthesis," Ed. J. I. G. Cadogan, Academic Press, New York (1979)

TL 2433 (1979) (enamines); 2671 (1980) (enamines); 23 4505 (1982) (allylic amines); 24 111 (1983); 28 5559 (1987) (alkylidene cyclopropanes); 29 2401 (1988); 30 4581 (1989); 31 2743 (1990); 32 2813, 4643 (1991); 34 1479 (1993) (enamides); 35 6733 (1994); 36 5719, 7905, 8477 (1995)

CC 100 (1981); 1196 (1987)

Tetr 37 3911 (1981)

JOC 46 459 (1981); 51 1264, 1269 (1986); 54 747, 1792 (1989); 60 6211 (1995)

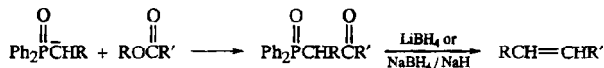
Ann 99 (1981)

CL 1143 (1982)

JACS 108 2662 (1986); 111 1157 (1989); 112 2998 (1990); 116 6207 (1994)

Chem Rev 89 863 (1989) (review)

SL 260 (1994)

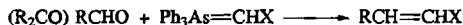


CC 100 (1981)

TL 24 111, 5293 (1983); 30 4581 (1989)

JOC 52 4303 (1987)

9. Arsenic Ylids



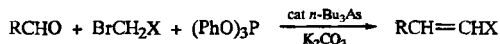
Org Prep Proc Int 14 373 (1982) (X = COCH₃)

TL 26 6447 (1985) (X = CHO); 28 2155 (X = CH=CHCOR, R = H, Me), 2159 (X = CONR₂, CHO, CH=CHCHO) (1987); 29 2647 (X = CH=CHCHO), 3949 (X = CONHR, CHO) (1988); 30 5263

[Ph₂As(CHPh)₂], 6023 (X = SPh) (1989); 34 5895 (1993) (X = CO₂R); 36 425 (1995)

[Ph₃As=C(SePh)CO₂Me]

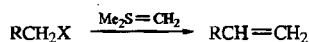
JOC 52 3558 (1987) (X = CHO); 54 3229 (1989) (X = CH=CH₂)



X = COR, CO₂R

JOC 54 2027 (1989)

10. Sulfur Reagents



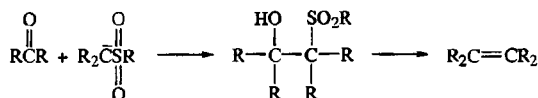
TL 35 5453 (1994)

LiCH₂SO₃CH₂CX₃ (X = F, Cl)/HOAc

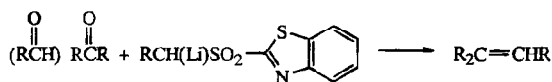
TL 31 981 (1990)

LiCH₂SONLiR/H₂O/Δ

JACS 88 5656 (1966); 90 5548, 5553 (1968)



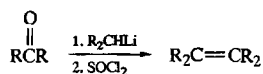
See page 283, Section 29.



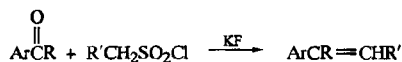
TL 32 1175 (1991)



SL 133 (1992)

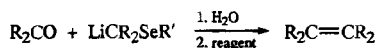


JOC 54 1375 (1989)



JOC 59 2898 (1994)

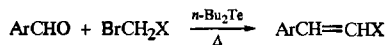
11. Selenium Reagents



Review: Tetr 36 2531 (1980)

For the reagents used to effect β-hydroxyselenide elimination, see page 286, Section 34.

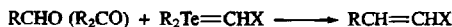
12. Tellurium Reagents



X = CO₂R, COR, CN

TL 28 801 (1987)

JOC 53 4862 (1988)



X

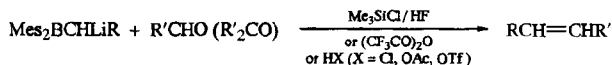
COPh JOC 53 4862 (1988)

CO₂R TL 24 2599 (1988)

JOC 53 4862 (1988)

CN JOC 53 4862 (1988)

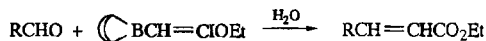
13. Boron Reagents



TL 24 635 (1983); 30 5647 (1989)

CC 297 (1987)

JACS 117 6142 (1995)



TL 30 5153 (1989)

14. Peterson Reaction (Oxysilane Elimination) and Related Reactions

Reviews:

Org Rxs 38 1 (1990)

SL 764 (1991)



JOC 33 780 (1968) (alkenes, vinylic sulfides and phosphines); 37 939 (vinylic sulfides and phosphonates), 1926 (ketene dithioacetals) (1972); 39 3264 (1974); 43 1947 (1978); 45 2013, 2713, 3451 (1980); 51 2863, 5111 (1986); 54 109, 1784 (X = SiMe₃), 1792 (X = SiMe₃) (1989); 55 4782 (1990) (2-fluoro-2-alkenoate esters); 56 638 (1991); 57 2554 (1992)

TL 1137 (1970); 1403, 4005 (X = CN) (1974); 7 (1976); 22 1575, 1595, 2751, 2923, 4705 (1981); 23 1279 (1982); 25 5177 (1984); 27 3729, 4189, 5829 (vinylic phosphonates) (1986); 28 259, 803 (1987); 29 25 (1988) (alkylidene cyclopropanes); 32 3285 (1991) (X = R); 33 4187 (1992); 34 5723 (1993); 35 6033 (1994) (2-fluoro-2-alkenoate esters)

CC 526 (1972) (ketene thioacetals); 537 (1975); 877 (1981); 98 (1986)

Angew Int 11 443 (1972) (ketene thioacetals); 15 161 (1976)

Ber 106 2277 (1973) (ketene thioacetals)

JACS 96 1620 (1974); 102 3964 (1980); 103 474 (1981); 104 5708 (1982); 106 3245, 3252 (1984); 107 2474 (1985) (X = OMe); 110 5172 (1988); 112 5276 (1990); 115 3966 (X = SPh), 10754 (1993)

CL 853 (1975) (X = SR); 1093 (1982) (X = CN)

Acct Chem Res 10 442 (1977) (review)

Chem Soc Rev 7 15 (1978)

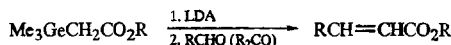
JCS Perkin I 26 (1979)

E. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), Chpt 12 (review)

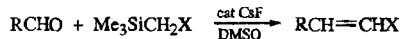
W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer Verlag, New York (1983), Chpt 6 (review)

Syn Commun 13 833 (1983)

Syn 384 (1984) (review); 734 (1986)



IOC 56 347 (1991)



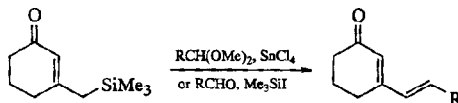
X = CO₂Et, CH=N-*t*-Bu, C(Me)=N-*t*-Bu

IOC 60 6582 (1995)

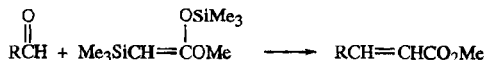


IOC 52 2314 (1987) (1-vinyl-1,2,4-triazoles); 55 2498 (1990)

TL 30 5841 (1989); 33 3903 (intramolecular) (1992) (both enamides)

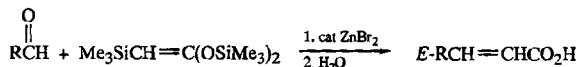


IOC 51 1932 (1986)

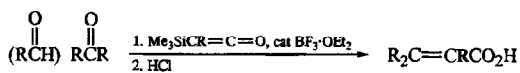


TiCl₄ / -78°C 95% *Z* olefin
AlCl₃ / 80°C 96% *E* olefin

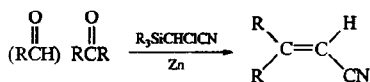
TL 22 1805 (1981); 29 4551 (1988)



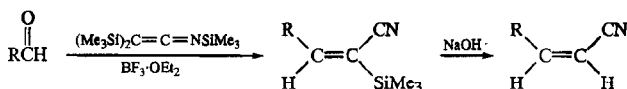
TL 29 4551 (1988)



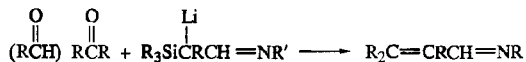
Syn Commun 25 15 (1995)



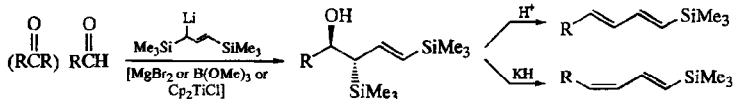
TL 31 2209 (1990)



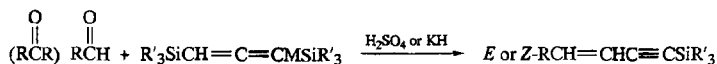
CC 56 (1982)



TL 7 (1976); 24 2481 (1983); 26 2391 (1985); 27 6177 (1986); 28 259 (1987); 29 281, 2275, 3895 (1988)
 JOC 45 2013 (1980); 50 2798 (1985)
 JACS 112 2998 (1990)



CC 969 (1982); 921 (1983)
 JOMC 264 207 (1984)
 TL 28 211 (1987)

M

Li

JACS 103 5568 (1981)
 TL 23 719 (1982)

MgX

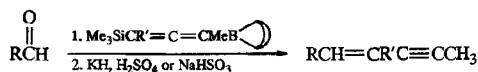
JACS 103 5568 (1981)

BR₂

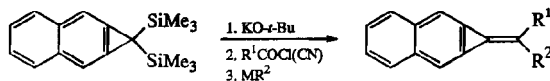
TL 34 8391 (1993)

Ti(OR)₃

CL 1093 (1982)
 TL 29 681 (1988)

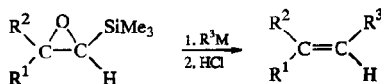


JOC 57 794 (1992)



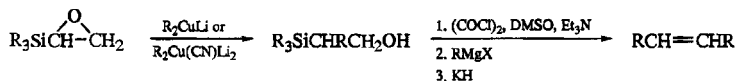
$R^1 = R, OR, NR_2; R^2 = H, R, OR, NR_2, CN$

TL 35 437 (1994)

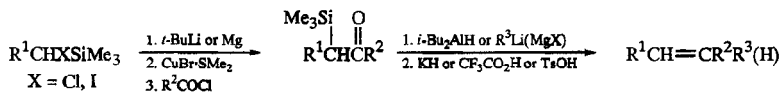


$R^3M = ArLi, LiC\equiv CR, LiCH_2CONR_2, Li-S(CH_2)_4-S, (H_2C=CH)_2Cu(CN)Li_2, Ar_2Cu(CN)Li_2$

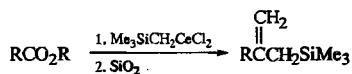
JOC 54 2043 (1989)



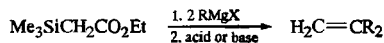
TL 34 3695 (1993)



JOC 56 638 (1991); 57 386 (1992)

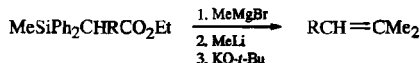


TL 28 6261 (1987); 29 5009 (1988)



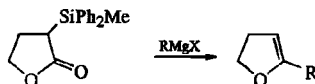
TL 23 1035 (1982)

SL 199 (1993)



JOC 49 4285 (1984)

Org Syn Coll Vol 8 474 (1993)



TL 23 271 (1982)

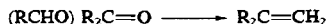


<u>X</u>	<u>Y</u>	
H	Ar	TL 34 7673 (1993)
H	CONMe ₂	TL 709 (1978)
H	RS, RSO ₂	BCSJ 55 1205 (1982)
RS	RS	Angew Int 11 443 (1972)

15. Isonitriles

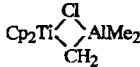


Angew Int 7 805 (1968)

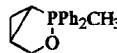
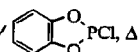
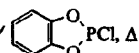
16. Miscellaneous Reactions

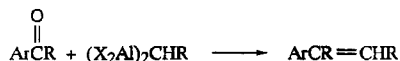


Review: Org Rxs 43 1 (1993) (Ti reagents)

ClCH ₂ I, CH ₃ Li/Li	CC 1665 (1986)
ClCH ₂ I or H ₂ CX ₂ (X = Br, I), Zn-Cu	JOMC 10 518 (1967); 12 263 (1968)
H ₂ CBr ₂ , Zn, TiCl ₄	TL 2417 (1978); 23 4293 (1982); 27 5467 (1986); 28 1893 (1987); 54 1483 (1989) JOC 45 2005 (1980); 48 2298 (1983); 50 5898 (1985); 52 34, 5583 (1987); 55 4860 (1990); 58 252 (1993) BCSJ 53 1698 (1980) Helv 65 293 (1982); 69 865 (1986) JACS 108 3513, 7791 (1986); 109 3147, 6937 (1987); 110 2242 (1988); 112 9272 (1990) Org Syn 65 81 (1987) CC 1008 (1987) Org Syn Coll Vol 8 386 (1993)
H ₂ CX ₂ (X = Br, I), Zn, Cp ₂ ZrCl ₂	TL 30 3927 (1989); 31 2875 (1990)
H ₂ Cl ₂ , Mg(Hg)	TL 5153 (1967) Tetr 26 1281 (1970) Ber 107 3486 (1974) JACS 107 5739 (1985)
H ₂ Cl ₂ , CrCl ₂	SL 607 (1994)
H ₂ Cl ₂ , Zn, Me ₃ Al	TL 2417 (1978); 26 5581 (1985) BCSJ 53 1698 (1980) JACS 107 4964 (1985) JOC 54 4114 (1989); 60 5693 (1995)

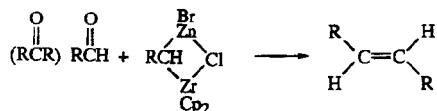
H_2Cl_2 , Zn, Me_3SiCl , cat PbCl_2	JOC 59 2668 (1994)
H_2Cl_2 , Zn, TiCl_4	TL 26 5579 (1985); 30 5857 (1989) JOC 56 1027 (1991) JACS 114 2635 (1992)
H_2Cl_2 , Zn, TiCl_4 , cat PbCl_2	JOC 59 2668 (1994)
H_2Cl_2 , Zn, $\text{Ti}(\text{O}-i\text{-Pr})_4$	TL 26 5581 (1985)
$\text{CH}_2(\text{AlClR})_2$ (R = Me, Et)	JOC 53 2829 (1988)
$\text{Cl}_2\text{AlCH}_2\text{TiCl}_3$	JOC 53 2829 (1988)
$\text{Cp}_2\text{TiCH}_2\cdot\text{ZnX}_2$	TL 24 2043 (1983)
Cp_2TiMe_2	JACS 112 6392 (1990); 116 6943 (1994) TL 31 6799 (1990); 36 6001 (1995) JOC 56 6156 (1991); 58 5918 (1993) Tetr 49 5067 (1993) CL 1503 (1993)
	JACS 100 3611 (1978); 102 3270 (1980); 113 2610, 2762 (1991); 114 2524 (1992) TL 23 3143 (1982); 25 5733 (1984); 27 6189 (1986); 28 3209 (1987) Pure Appl Chem 55 1733 (1983) (review) JOC 50 1212, 2386 (1985); 52 1780 (1987) Org Rxs 43 1 (1993) (review)
	TL 25 5733 (1984)
$\text{Cl}_2\text{Mo}(\text{Me})=\text{CH}_2$	Angew Int 23 532 (1984) TL 27 5355 (1986)
$\text{ClMo}(\text{Me})_2=\text{CH}_2$	Angew Int 23 532 (1984)
	TL 27 5355 (1986) Ber 126 89 (1993)
$\text{Zn}(\text{CH}_2\text{ZnBr})_2\cdot\text{THF}$, TiCl_4	JOC 60 5102 (1995)
$\text{Me}_3\text{SiCH}_2\text{Li}/\text{KH}$	JOC 53 5885 (1988); 56 7237 (1991) SL 269 (1992)
$\text{Me}_3\text{SiCH}_2\text{Li}$, CeCl_3/HF or KH	JOC 52 281 (1987) JACS 115 3855 (1993)
$\text{Me}_3\text{SiCH}_2\text{Li}(\text{MgX})/\text{HCl}$	JOC 33 780 (1968); 57 3347 (1992) TL 4193 (1973); 21 3451 (1980); 27 4873 (1986) Acct Chem Res 10 442 (1977)
$\text{Me}_3\text{SiCH}_2\text{Li}(\text{MgX})/\text{CH}_3\text{COCl}$	JOC 39 3264 (1974)
$\text{Me}_3\text{SiCH}_2\text{Li}(\text{MgX})/\text{SOCl}_2$	JOC 39 3264 (1974) Tetr 50 3235 (1994)
$\text{Me}_3\text{SiCH}_2\text{MgCl}/\text{H}_2\text{O}/\text{NaH}$	JOC 51 5311 (1986)
$\text{Me}_3\text{SiCH}_2\text{MgCl}/\text{H}_2\text{O}/(\text{CO}_2\text{H})_2$	JOC 52 3745 (1987)

$\text{Me}_3\text{SiCH}_2\text{MgX}/\text{H}_2\text{O}/\text{BF}_3\cdot\text{OEt}_2$	JOC 55 1363 (1990)
$\text{Me}_3\text{SiCH}_2\text{MgCl}$, $\text{CeCl}_3/\text{H}_2\text{SO}_4$	JOC 60 833 (1995)
$\text{Me}_3\text{SiCH}_2\text{PO}(\text{OMe})_2/\Delta$	CL 1385 (1978)
$\text{Me}_3\text{SiCH}_2\text{TiCl}_3$ (RCHO only)	TL 22 5031 (1981)
$\text{Me}_3\text{SiCH}_2\text{CrCl}_2/\text{H}_3\text{O}^+$ (RCHO only)	TL 22 5031 (1981)
$[(\text{Me}_3\text{Si})_2\text{N}]_2\text{UCH}_2\text{SiMe}_2\text{NSiMe}_3$	JOC 52 688 (1987)
$\text{Me}_3\text{GeCH}_2\text{TiCl}_3$ (RCHO only)	TL 22 5031 (1981)
XCH_2Li ($\text{X} = \text{Ph}_3\text{Pb}$, Ph_3Sn , Ph_2Sb)/ Δ or H^+	TL 4399 (1978)
$\text{H}_2\text{C}=\text{PPh}_3$	Org Rx 14 270 (1965) (review) JOC 46 1105 (1981); 53 2866 (1988) Org Syn 64 164 (1985) Syn Commun 15 855 (1985) Org Syn Coll Vol 7 258 (1990)
	TL 27 1909 (1986)
$\text{Ph}_2\text{POCH}_2\text{Na}$	Ber 91 61 (1958)
$(\text{Me}_2\text{N})_2\text{POCH}_2\text{Li}$	JACS 88 5653 (1966) Org Rx 25 73 (1977) (review)
$\text{PhSCH}_2\text{Li}/\text{TiCl}_4\text{-LiAlH}_4\text{-3}^\circ$ amine	CL 871 (1975)
$\text{PhSCH}_2\text{Li}/$  PCl_2, Δ	TL 737 (1972)
$\text{PhSCH}_2\text{Li}/(\text{PhCO})_2\text{O}/\text{Li}, \text{NH}_3$	JACS 94 4728 (1972)
$\text{PhSCH}_2\text{Li}/(\text{PhCO})_2\text{O}/\text{TiCl}_4, \text{Zn}$	CL 1523 (1974)
$\text{PhSOCH}_2\text{Li}/$  PCl_2, Δ	TL 649 (1972)
$p\text{-MeC}_6\text{H}_4\text{SO}_2\text{CH}_2\text{MgI}/\text{NaBH}_4/\text{electrolysis}$	CL 69 (1978)
$\text{PhSO}(=\text{NMe})\text{CH}_2\text{Li}/\text{Al}(\text{Hg}), \text{HOAc}$	JACS 95 6462 (1973); 101 3602 (1979); 103 7667 (1981); 106 4547 (1984)
$\text{PhP}(=\text{S})(\text{NMe}_2)\text{CH}_2\text{Li}/\text{MeI}, \text{py}$	JACS 104 7041 (1982); 106 8217 (1984)
$m\text{-CF}_3\text{C}_6\text{H}_4\text{SeCHLi}(\text{OMe})/\text{MsCl}, \text{Et}_3\text{N}$	JACS 101 6638 (1979)

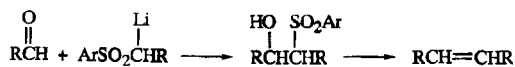


$\text{X} = \text{Cl}, \text{Et}$

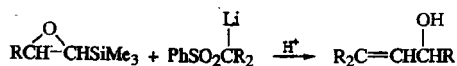
JOC 53 2829 (1988)



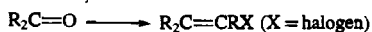
JACS 113 9888 (1991)



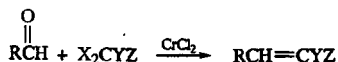
See page 283, Section 29 and page 284, Section 30.



See page 351, Section 1.



See page 709, Section 1.



X = Cl, Br, I

Y, Z

H, H

SL 607 (1994)

H, alkyl

JACS 109 951 (1987); 113 4607 (1991)

JOC 57 5596 (1992)

H, SPh

TL 28 1443 (1987)

H, B(OR)₂

SL 963 (1995)

H, SiMe₃

TL 28 1443 (1987)

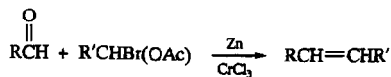
H, SnR₃

TL 33 5603 (1992); 35 2231 (1994); 36 763 (1995)

SiMe₃, SiMe₃

TL 35 9469 (1994)

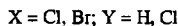
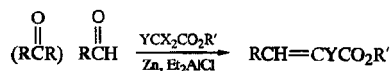
For Y and/or Z = halogen, see page 709, Section 1.



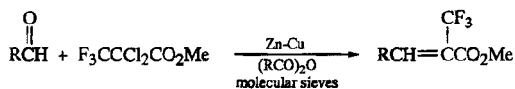
SL 837 (1993)



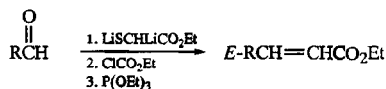
SL 1071 (1995)



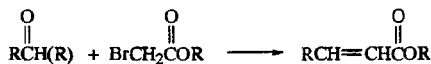
BCSJ 53 1698 (1980)



TL 32 339 (1991)



Syn 127 (1983)

*n*-Bu₃P, Zn

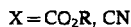
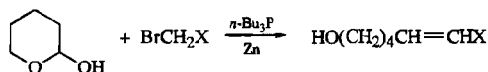
TL 29 6119 (1988)

n-Bu₃P, cat Pd(PPh₃)₄

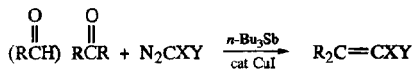
TL 32 513 (1991)

n-Bu₃Sb

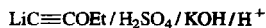
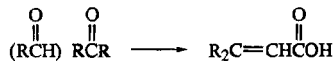
TL 27 2903 (1986)



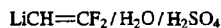
TL 36 6467 (1995)



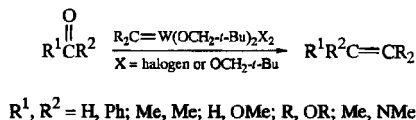
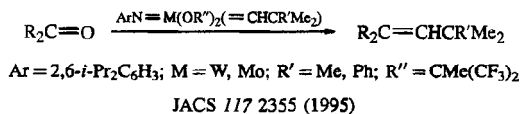
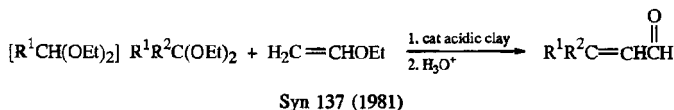
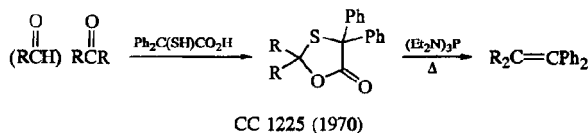
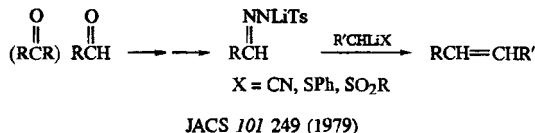
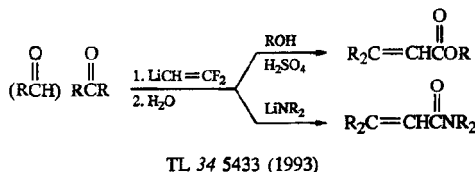
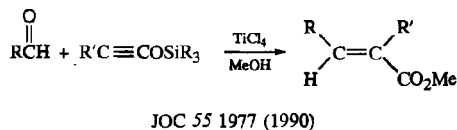
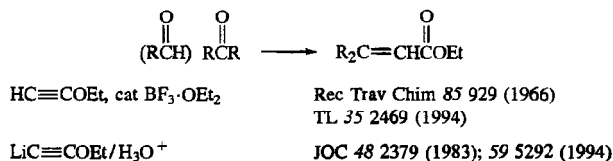
TL 31 5897 (1990)

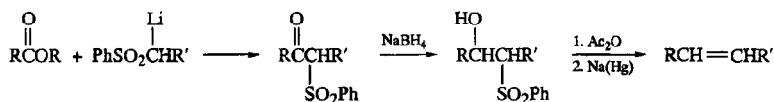


JACS 108 2691 (1986)



TL 34 5433 (1993)



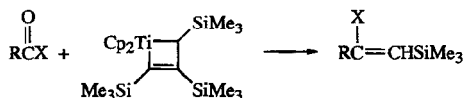


JACS 108 284 (1986)

See page 283, Section 29, and page 284, Section 30, for other reagents to effect elimination.

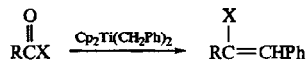


SL 665 (1992)

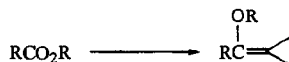
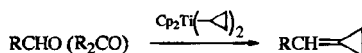


X = H, R, OR, SR

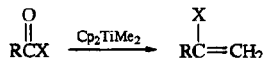
TL 36 3619, 6001 (1995)

X = H, R, OR, NR₂

JOC 57 1327 (1992)



TL 34 943 (1993)



X
OR

JACS 112 6392 (1990); 115 5957 (1993); 117 6394 (1995)

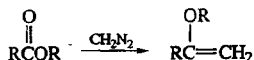
TL 31 6799 (1990); 34 1721 (1993)

JOC 56 3207, 6156 (1991); 59 6167 (1994); 60 3787 (1995) (lactone)

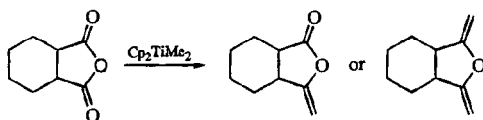
Tetr 47 1655 (1991)

OSiMe₃, SPh, SePh, O₂CR, NR₂, SiMe₃

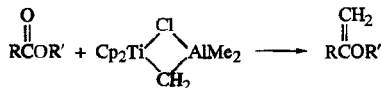
TL 36 2393 (1995)



TL 28 3011 (1987)



JOC 59 494 (1994)



TL 1439 (1975); 23 3143 (1982); 25 395 (1984); 28 4773 (1987); 29 4333 (1988); 30 6081 (1989); 35 2537 (1994)

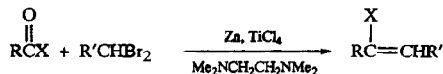
JACS 102 3270 (1980); 106 6868 (1984); 107 7352 (1985); 110 5768 (1988); 113 2610, 2762 (1991); 114 6354 (1992)

Pure Appl Chem 55 1733 (1983)

JOC 48 1829 (1983); 50 1212, 2386 (1985); 51 5458 (1986); 55 1703 (1990); 57 4142 (1992); 59 4029 (1994); 60 6025 (1995)

Org Rxs 43 1 (1993) (review)

Org Syn Coll Vol 8 512 (1993)



$\frac{X}{|}$

OR

JOC 52 4410 (1987); 55 1813, 5196, 5719 (1990); 57 4567 (1992); 59 4029, 5758 (1994)

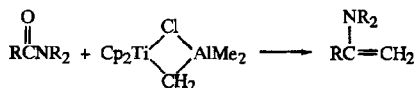
TL 29 1065, 3357 (1988)

SL 27 (1989); 209 (1990)

Org Rxs 43 1 (1993)

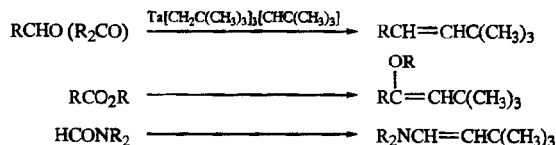
SR, NR₂

TL 30 211 (1989)

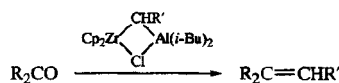


JOC 50 1212 (1985)

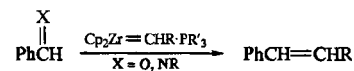
Org Rxs 43 1 (1993) (review)



JACS 98 5399 (1976)



JACS 105 640 (1983)

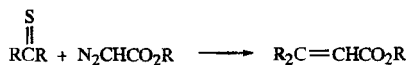


JACS 106 8300 (1984)

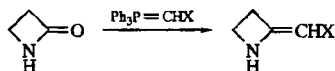


X = F, Cl

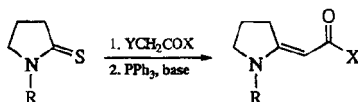
See page 732, Section 6.



See page 271, Section 17.

X = CO₂R, CN

SL 51 (1993)



X = R, OR; Y = halogen, OTf

JCS 916 (1955)

Helv 54 710 (1971)

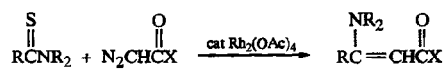
Ann 1309 (1979)

JOC 45 1868 (1980); 46 3230 (1981); 47 4403 (1982); 48 1439 (1983); 55 5025 (1990); 59 1058, 3575 (1994)

TL 24 829 (1983); 36 3715, 7787 (1995)

JACS 106 4539 (1984); 117 5399 (1995)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 3.7, p 865



X = alkyl, OR

See page 271, Section 17.

5. METAL-PROMOTED COUPLING REACTIONS

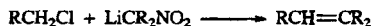
See also page 234, Section 6, and page 403, Section 6.

1. Alkali Metal Reagents

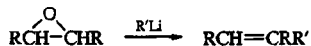
Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.6, p 241

For transition metal-catalyzed cross-coupling of organolithium compounds, see the appropriate transition metal.

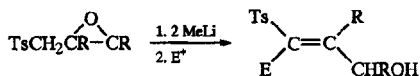
For other ways of generating vinylic lithium reagents, see page 373, Section 9, and page 379, Section 11.



TL 35 3305 (1994)

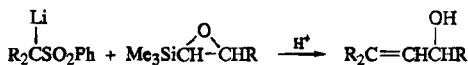


TL 35 7943 (1994)

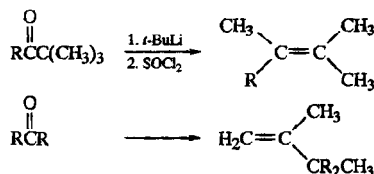


$\text{E}^+ = \text{H}_2\text{O}, \text{RX}, \text{RCHO}$

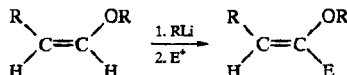
JOC 54 1491 (1989)



TL 29 2497 (1988); 30 2845 (1989)



JOC 55 1792 (1990)


 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCO}_2\text{R}, \text{RCN}, \text{CO}_2, \text{ClCO}_2\text{R}, \text{RNCO}, \text{R}_3\text{SiCl}, \text{R}_3\text{SnCl}$

Ann 763 208 (1972)

Syn 888 (1974); 748 (1982)

JACS 96 7125 (1974); 97 3822 (1975) (cuprate); 103 5259 (1981); 113 5073, 5337, 5775 (1991); 114 9419 (1992)

TL 4187 (1977); 24 3905 (1983) (cuprate); 27 5975, 6201 (1986); 29 1993, 2867 (1988); 34 5693, 6127 (1993)

Compt Rend C 284 281 (1977)

Tetr 37 3997 (1981)

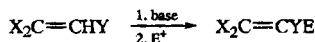
Syn Commun 12 579 (1982)

JOC 51 4492 (1986); 53 5672 (1988); 54 4721 (1989); 57 1179, 3947 (1992); 60 2526 (1995)

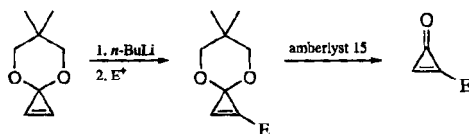
Heterocycles 30 765 (1990)

SL 269 (1992)

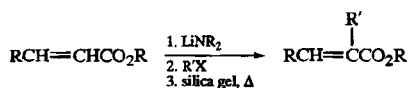
Org Syn Coll Vol 8 19 (1993)



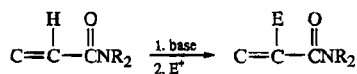
<u>X</u>	<u>Y</u>	<u>E</u> ⁺	
H	OCONEt ₂	RX, epoxide (BF ₃ ·OEt ₂ or CuCN·2LiCl), RCOCl, RNCO, (PhSe) ₂ , ArSO ₂ F, R ₃ SiCl, ArBr (Pd cat), RCH=CHBr (Pd cat)	JOC 55 5680 (1990)
F	OCONEt ₂	H ⁺ , RCHO, R ₂ CO, CO ₂ , R ₃ SiCl, R ₃ SnCl	SL 483 (1992)
	OMEM	RCHO, R ₃ SiCl	TL 31 3931 (1990)


 $\text{E}^+ = \text{RX}, \text{RCH}=\text{CHI} \text{ or } \text{ArI} [\text{ZnCl}_2, \text{cat Pd}(\text{PPh}_3)_4], \text{RCHO}, \text{R}_2\text{CO}$

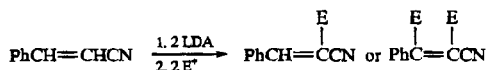
JOC 54 4727 (1989)



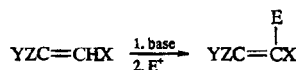
CC 1410 (1987)

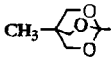




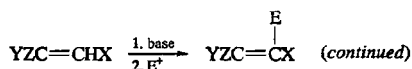
See page 1778, Section 4.

 $\text{E}^+ = \text{MeOD}, \text{RX}, \text{RCHO}, (\text{MeS})_2$

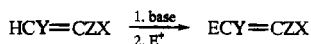
JOC 52 3825 (1987)



<u>X</u>	<u>Y</u>	<u>Z</u>	<u>E⁺</u>	
Cl		H	RX, RCHO, R ₂ CO, 4-alkanolide	TL 28 2335 (1987)
NR ₂	PO(OR) ₂	H, Me	RX, ClCO ₂ R	TL 30 4787 (1989)
SR	SR	H	D ⁺ , CH ₃ OSO ₂ F, RCHO, (RS) ₂	TL 3583 (1977)
SPh		H, Me	D ₂ O, 1° RI, RCHO	J Chem Res (S) 48 (1982)
SOR	SR SiR ₃	H H	MeOD, MeI, (MeS) ₂ RCHO	TL 4277 (1979) TL 34 6587 (1993)
SO ₂ Ph	OMe OR	H H, Me	CH ₃ OD, MeI, R ₂ CO D ₂ O, RX, RCHO, R ₂ CO	JOC 52 4760 (1987) TL 28 4127 (1987)
	SMe	SMe	RX, RCHO, enone (1,4-addition), epoxide, RCOCl, RCH=NR, RNCO, Me ₂ SiCl	JOC 54 1757 (1989)
Ts		H	D ₂ O, RX, RCHO, R ₂ CO	TL 34 2003 (1993)
	CH(OEt) ₂	H	D ₂ O, RX, RCHO, RCOCl, R ₃ SiCl	TL 34 5445 (1993)



<u>X</u>	<u>Y</u>	<u>Z</u>	<u>E</u> ⁺	
	C(Me)(OMe) ₂	H	D ₂ O, RX, RCHO, RCOCl, Ac ₂ O, ClCO ₂ R, RNCO, Me ₃ SiCl, RSSR	JOC 53 4708 (1988)
CO ₂ R	Ph	Ph	D ₂ O, MeI, RCHO, R ₂ CO, CO ₂ , 2-alkenenitrile (1,4-addition)	JCS Perkin I 1329 (1981)
	OMe	R	D ⁺ , RCHO, R ₂ CO, RCOX, (RCO) ₂ O, RCO ₂ R, (MeS) ₂	TL 23 1793 (1982) Tetr 39 2043 (1983)
		CO ₂ R	D ⁺ , RCHO, Ac ₂ O, (MeS) ₂	Tetr 39 2043 (1983)
	NRCOR	H	D ₂ O	TL 22 4259 (1981)
CN	OEI	H	D ₂ O	TL 22 4259 (1981)
	NR ₂	H	MeOD, RI, RCHO	Angew Int 16 853 (1977)
	SR	H	MeOD, MeI, RCHO, (RS) ₂	TL 4277 (1979)
	Ph	H	D ⁺ D ⁺ , MeI, RCHO, R ₂ CO, enone (1,4-addition)	TL 4273 (1979) Syn 797 (1979) Tetr 37 2143 (1981)
		Ph	RI, R ₂ CO, CO ₂ , 2-alkenenitrile (1,4- addition)	JCS Perkin I 1228, 1232 (1978)
	Ar	H	D ⁺ , MeI, (MeS) ₂	Tetr 39 2043 (1983)



Review: Bull Soc Chim Belg 92 825 (1983)

<u>X</u>	<u>Y</u>	<u>R</u>	<u>E</u> ⁺	
COR	NR ₂	H	D ⁺	TL 4273 (1979)
CO ₂ H	H	OMe	D ⁺ , RCHO	Syn 160 (1985)
	Br	n-Bu	Ac ₂ O, RCHO	JOC 50 2195 (1985)
CO ₂ R	Ph	H	R ₂ CO	JCS Perkin I 1329 (1981)
	OR	H	D ⁺ , RCHO, R ₂ CO, RCO ₂ R, (RS) ₂ , 2-alkenoate ester (2-cyclopentenone), vinyl sulfone (2-cyclopentenone)	TL 4273 (1979); 22 4259 (1981); 23 1793 (1982); 33 8035 (1992); 34 4161 (1993) Tetr 39 2043 (1983) SL 191 (1990)

		Me	RCHO	SL 429 (1992)
		OMe	PhNCO, PhNCS	Ber 115 2674 (1982)
		OR	RCHO	Syn 748 (1982)
	SPh	Me	2-alkenoate ester (2-cyclopentenone)	CL 815 (1982)
				CC 496 (1982)
	NR ₂	H	D ⁺	TL 4273 (1979)
			RCHO, HCO ₂ R,	Angew Int 17 204 (1978)
			RCO ₂ R (all alkanolides), 2-alken-1-one, 2-alkenoate ester, 2-alkenenitrile (all 2-cyclopentenones)	SL 191 (1990)
		OMe	CO ₂ , RNCO, RNCS	Ber 115 2674 (1982)
			RCHO, PhNCO, PhNCS	Ber 115 2674 (1982)
		SMe	D ⁺ , RCHO	Syn 748 (1982)
				TL 22 4259 (1981)
	CO ₂ R	OMe	D ⁺ , RCHO, Ac ₂ O, (MeS) ₂	Syn 748 (1982)
				Tetr 39 2043 (1983)
CONHR	H	OMe	D ⁺ , RX, RCHO, Me ₃ SiCl, RSSR	Syn 160 (1985)
	SPh	OCH ₂ Ph	RCHO	TL 27 5591 (1986)
CONR ₂	Ar	H	D ⁺ , MeI, RCHO	Tetr 39 2043 (1983)
	OR	H	D ⁺	TL 22 4259 (1981)
	NR ₂	H	D ⁺	TL 4273 (1979); 22 4259 (1981)
			D ⁺ , RI, RCO ₂ R	Angew Int 15 171 (1976)
			ArCR=X (X=O, NPh)	Syn 869 (1977)
			CO ₂ , RNCO, RNCS	Ber 115 2674 (1982)
CN	OR	Me	D ⁺	TL 22 4259 (1981)
	NR ₂	H	D ⁺	TL 4273 (1979)
			D ⁺ , RI, RCHO	Angew Int 16 853 (1977)
		SMe	D ⁺	TL 22 4259 (1981)



X

halogen

Syn 434 (1975)
JOC 52 2674 (1987)
TL 33 6183 (1992)

SPh

JOC 54 1836 (1989)

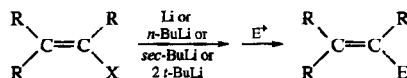
SO₂R

TL 25 4851 (1984); 32 4579, 4583 (1991)
JOC 54 1635, 1836 (1989)



n=2, 3

JOC 58 5976 (1993)



X = halogen; E⁺ = D₂O, RX, I₂, Me₃SiCl, RSSR, R₂CO, RCHO, ROOR, ClCO₂R, RCH(O)₂CH₂, DMF

TL 3809 (1974); 4839 (1976); 4661 (1978); 22 3745 (1981); 28 5145 (1987)

Syn 434 (1975)

Ber 111 2785 (1978)

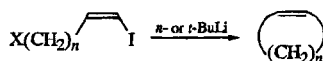
Syn Commun 9 831 (1979)

Organomet 1 667 (1982)

JOC 52 3860, 4495 (1987); 59 6090 (1994)

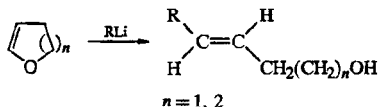
JACS 110 5567 (1988) (1,1-diiodoalkenes); 113 3096 (1991); 114 9782 (1992)

SL 645 (1994)

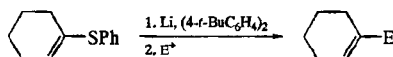


JACS 105 6344 (1983) (n = 2-4); 106 6105 (1984) (n = 3-5); 110 5383 (1988) (n = 1-5); 111 3336 (1989) (n = 2)

TL 26 5671 (1985) (n = 1); 28 5793 (1987) (n = 3, 4)

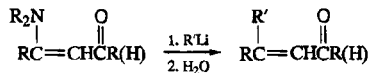


See page 1061, Section 4.3.



E⁺ = RX, RCHO, R₂CO, HCONMe₂, Me₃SiCl

JOC 55 4784 (1990)

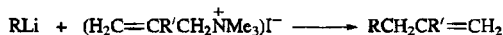


JOC 43 4248 (1978)

CC 75 (1986)

TL 29 2861 (1988)

See also page 359, Section 2, for analogous reactions.

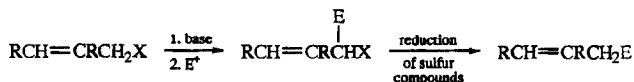


JOC 52 3683 (1987)




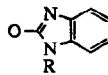
X = OR, NHR



TL 30 3837 (1989)

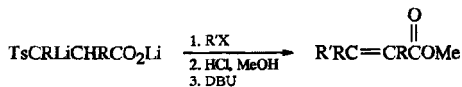


Review: Org Rxs 27 1 (1982)

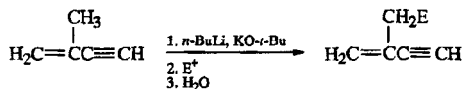
See also page 490, Section 3.9 and page 492, Section 3.11.

<u>X</u>	<u>E⁺</u>	
H	H ₂ O, Me ₃ SiCl MeI 1° RBr 1° RBr, FB(OMe) ₂ ·OEt ₂ 3° RBr RX RX, RCHO, R ₂ CO D ₂ O, RX, R ₂ CO, Me ₃ SiCl D ₂ O, RX, RCHO, R ₂ CO, CO ₂ , Me ₃ SiX, Me ₃ SnCl RX, RCHO, R ₂ CO, O ₂ , (RS) ₂  RCHO	TL 669 (1973) Helv 57 1567 (1974) JOC 55 2742 (1990) TL 34 5441 (1993) JACS 109 3391 (1987) JOC 54 2117 (1989); 59 2025 (1994) TL 4115 (1973) JACS 105 6350 (1983) TL 3047 (1975) JACS 101 3340 (1979) Chem Pharm Bull 32 4632 (1984) Helv 57 1567, 2261 (1974) JACS 108 3385 (1986) JOC 60 7051 (1995)
C	1° RBr LiCuCl ₂ /RI	JACS 114 2245 (1992) JOC 54 2117 (1989)
Cl	RX	JOC 46 1504 (1981) SL 769 (1990)
OR	RCHO, R ₂ CO	JACS 96 5560 (1974) (via Zn compounds) TL 833 (1979)
OSiR ₃	RCHO, R ₂ CO R ₃ SiCl	JOC 41 3620 (1976) JOC 43 2551 (1978)
	RCHO	CL 1279 (1979)
NHCO ₂ -i-Bu	RCHO or R ₂ CO, ZnCl ₂	TL 34 3043 (1993)
SH	RCHO, R ₂ CO	Ber 112 1420 (1979) (via Mg compounds)
SAr	RX	TL 5629 (1968); 3707 (1969); 24 5531 (1983); 27 2157 (1986); 30 4867 (1989) Proc Natl Acad Sci USA 68 1294 (1971) Tetr 27 5861 (1971) CC 1311 (1972) JACS 95 4444 (1973); 103 4615 (1981) Helv 57 2261 (1974) Syn 129 (1974) JOC 45 4097 (1980); 59 3113 (1994) TL 28 5665 (1987); 29 1143 (1988) TL 33 7445 (1992); 34 2799 (intramolec- ular), 7487 (1993)
	epoxide RCHO, R ₂ CO	

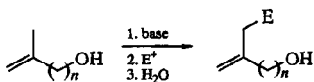
<u>X</u>	<u>E</u> ⁺	
	$\text{H}_2\text{C}=\text{CHCONR}_2$ $\text{PhN}=\text{NPh}$	JOC 52 218 (1987)
	RX	JOC 57 5060 (1992)
	RX	BCSJ 44 2285 (1971)
SO_2Ar	RX	BSCF 746 (1973) JOC 39 2135 (1974); 51 5100 (1986); 57 4598, 7226 (1992) JCS Perkin I 761 (1981) CL 25 (1981); 725 (1983) JACS 107 396 (1985) TL 27 2683 (1986); 28 187, 3193, 6045 (1987); 29 4591 (1988); 35 8867 (1994) CC 1761 (1986); 1036 (1987) TL 34 2867 (1993) BSCF 513 (1976) TL 29 4811 (1988) TL 35 8867 (1994) TL 28 6045 (1987)
	Me_3SiCl epoxide	TL 34 2867 (1993) BSCF 513 (1976) TL 29 4811 (1988) TL 35 8867 (1994) TL 28 6045 (1987)
	RCHO enone (1,4-addition)	TL 28 6045 (1987)
SC(S)NR_2	RX	Syn 100 (1975) CL 249 (1975) JACS 105 2909 (1983) TL 4027 (1975) Chem Pharm Bull 30 3852 (1982)
	RX, RCHO, R_2CO , epoxide RCHO, R_2CO	Chem Pharm Bull 30 3852 (1982)
SePh	RX	JOC 52 3759 (1987)
$\text{SiMe}_2\text{N}(i\text{-Pr})_2$	RCHO (ZnCl_2)	JOC 52 957 (1987)
SiMe_3	RX	TL 29 4991 (1988)



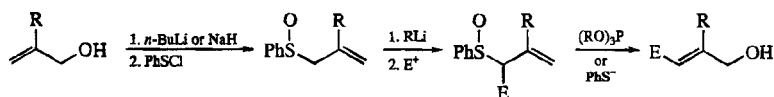
JOC 59 3202 (1994)

 $\text{E}^+ = \text{RX, epoxide, RCHO, R}_2\text{CO, RCONR}_2, \text{CO}_2, (\text{MeS})_2, \text{RSCN}$

JOC 52 5261 (1987)



n	E^+	
1	RX	TL 2215 (1974) JACS 115 9421 (1993) Syn Commun 13 237 (1983) TL 111 (1978) JACS 103 5972 (1981) Org Syn 62 58 (1984) Org Syn Coll Vol 7 266 (1990)
	epoxide RCHO, R ₂ CO Me ₃ SiCl	
2	ROT's	JACS 110 1624 (1988)

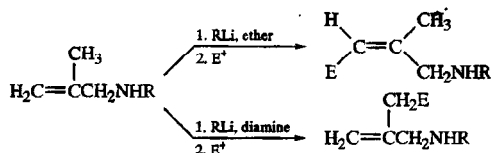
 E^+

RX

JACS 93 4956 (1971); 94 3672 (1972)
CC 702 (1972)
TL 1385, 1389 (1973)
JOC 38 2245 (1973)
Acct Chem Res 7 147 (1974)

epoxide

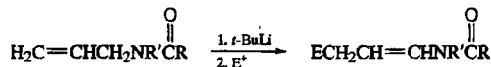
Syn Commun 11 723 (1981)


 $E^+ = \text{D}_2\text{O}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCH}=\text{NR}, \text{CO}_2, (\text{RO})_2\text{CO}$ (both 2-alkene-4-lactams) RSSR

TL 29 4859 (1988); 33 7573 (1992)

CC 1135 (1988)

J Chem Res (S) 200 (1989)

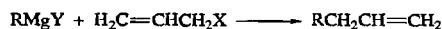

 $E^+ = \text{D}_2\text{O}, \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{R}_3\text{SiCl}, \text{R}_3\text{SnCl}$
TL 3407 (1978) ($R' = \text{H}$)

JOC 54 458 (1989)

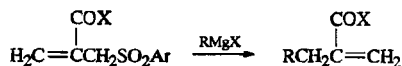
2. Grignard Reagents

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.6, p 241

For transition metal-catalyzed cross-coupling reactions of Grignard reagents, see the appropriate transition metal.

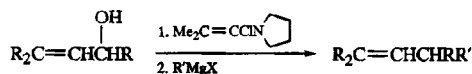


<u>X</u>	<u>R</u>	
Cl	1° alkyl 1° alkyl, Ph	Org Mag Res 10 192 (1977) Ind Eng Chem 33 115 (1941)
Br	Me n-Bu, Ph t-Bu c-C ₅ H ₁₁ 1° alkyl, Ph	JOC 14 505 (1949) Helv 17 351 (1934) JACS 55 4555 (1933) JACS 68 1101 (1946) JOC 53 2304 (1988)
I	1° alkyl	JOC 57 5247 (1992)
OR	1° alkyl, aryl	JACS 75 5408 (1953)
OPO(OEt) ₂	1° alkyl, allyl, benzyl, aryl, alkynyl	CC 285 (1982)
+ NMe ₃ I ⁻	Me, Ph	JOC 52 3683 (1987)



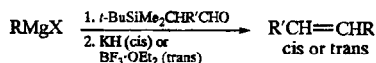
X = OR, NHR; R = 1° alkyl, allyl, vinyl, aryl

TL 30 3837 (1989)



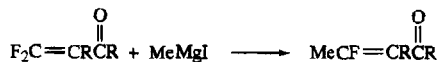
R' = 1° alkyl, Ph

TL 24 5745 (1983)

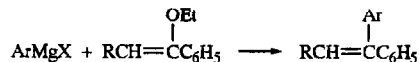


cis or trans

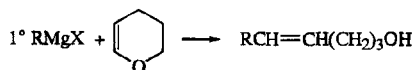
JACS 103 6251 (1981)



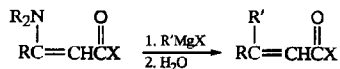
SL 186 (1993)



JACS 73 1663 (1951)



See page 1061, Section 4.3.



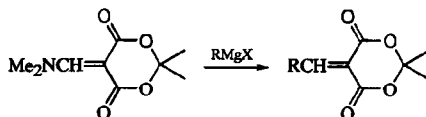
X = H, R, NR₂

Ber 64 2543 (1931)

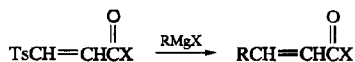
BSCF 515 (1960); 1294 (1964)

TL 26 1819 (1985); 34 4667 (1993)

See also page 351, Section 1, for analogous reactions.

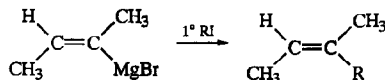


Syn Commun 10 661 (1980)

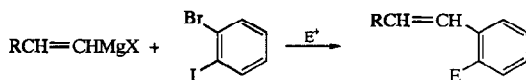


X = OR, NR₂; R = allyl, vinylic, alkynyl

TL 30 173 (1989)



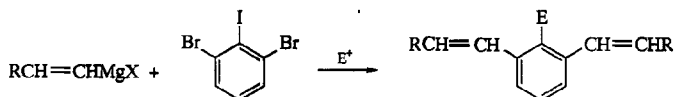
TL 3225 (1976)



E⁺ = H₂O, HCONR₂, CO₂, I₂

JOC 52 4311 (1987)

TL 29 885 (1988)



E⁺ = H₂O, MeI, I₂

JOC 52 4311 (1987)

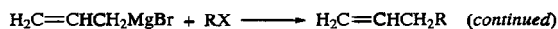
TL 29 881, 885 (1988)



X
Br
I

JOC 59 7876 (1994)

TL 35 5113 (1994)



X

OTs

TL 1181 (1977)

JACS 109 7488 (1987)

JOC 53 2968 (1988)

OPO(OR)₂

SL 841 (1995) (chiral)

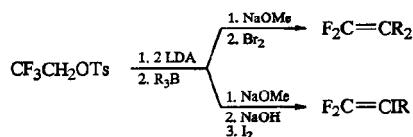


R' = Me, PhCH₂, allylic, propargylic

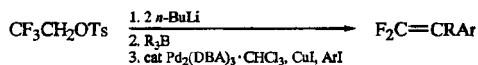
JACS 115 5879 (1993)

3. Boron Reagents

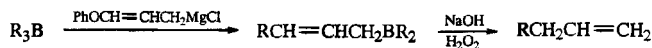
See also page 392, Section 22 and page 421, Section 2.8.



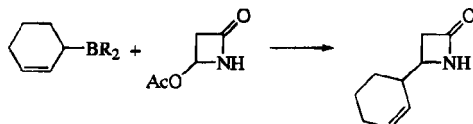
TL 30 6379 (1989)



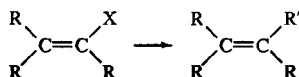
TL 33 3779 (1992)



Syn Commun 12 813 (1982)

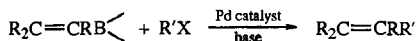


JACS 117 9604 (1995)



Review: Chem Rev 95 2457 (1995)

X	Reagents	
halogen	$\text{R}'\text{B}-\text{O}$, cat $\text{Pd}(\text{PPh}_3)_4$, NaOH	TL 31 4981, 5541 (1990) JACS 114 360 (1992) JOC 57 5844 (1992) JOC 43 1279 (1978) Syn 945 (1980)
	$n\text{-BuLi}/\text{R}'_3\text{B}/\text{I}_2$	TL 27 6379 (1986); 29 3983 (1988); 30 4637 (1989); 33 2571 (1992) (intramolecular); 34 5031 (1993); 36 6101 (1995) JACS 111 314 (1989); 115 11014 (1993); 117 5958 (1995) Pure Appl Chem 63 419 (1991) SL 687 (1991); 727 (1992); 573 (1993); 607 (1994)
	$\text{R}'_3\text{B}$ or $\text{R}'\text{B}-\text{O}$ ($\text{R}' = 1^\circ$ alkyl), Pd catalyst, base	BCSJ 61 3008 (1988) JOC 55 6184 (1990); 56 4821 (1991) SL 715 (1992); 573 (1993) TL 34 4485 (1993)
	$\text{ArB}(\text{OH})_2$, Pd catalyst, base	BCSJ 61 3008 (1988) TL 32 5881 (1991)
	$\text{ArB}(\text{OR})_2$, cat $\text{Pd}(\text{PPh}_3)_4$, Ti_2CO_3 $\text{Het-B}(\text{OMe})_2$, cat $\text{Pd}(\text{PPh}_3)_4$	BCSJ 61 3008 (1988) TL 32 5881 (1991)
	$\left[\text{RC}\equiv\text{C}-\text{B}(\text{OCH}_3)_2 \right] \text{Li}$, cat $\text{Pd}(\text{PPh}_3)_4$	See page 589, Section 2.
OTf	$\text{RB}(\text{OH})_2$ ($\text{R} = \text{Me}, \text{Ph}$), cat $\text{PdCl}_2(\text{PhCN})_2$, cat Ph_3As , base	TL 36 5669 (1995)
	$\text{RB}-\text{O}$, cat $\text{Pd}(\text{PPh}_3)_4$ or $\text{PdCl}_2(\text{dppf})$, K_3PO_4	SL 221 (1990) JOC 58 2201 (1993)
	$\text{ArB}(\text{OH})_2$, Pd catalyst, base	TL 34 2437, 3211 (1993); 36 3099, 4869 (1995) JOC 58 2201 (1993); 60 2658 (1995) Acta Chem Scand 47 221 (1993) (review)
	$\text{Het-B}(\text{OH})_2$, cat $\text{Pd}(\text{PPh}_3)_4$, LiCl, Na_2CO_3	TL 34 2235 (1993)
	$\text{Het-B}(\text{OR})_2$, cat $\text{Pd}(\text{PPh}_3)_4$	SL 221 (1990) TL 32 5881 (1991)
	NaBAR_4 , cat $\text{Pd}(\text{PPh}_3)_4$, Et_3N	TL 33 4815 (1992)
	$(\text{R}_3\text{BMe})\text{Li} + \text{BrCH}=\text{CHCO}_2\text{Et} \xrightarrow{\text{CuI}}$	$\text{RCH}=\text{CHCO}_2\text{Et}$ retention
	TL 3369 (1977)	
	$\text{RCH}=\text{CBr}_2 + \text{Cyclohexyl-B}(\text{CH}_2)_5\text{B-Cyclohexyl} \xrightarrow{\text{Pd catalyst}}$	$\text{RCH}=\text{Cyclohexyl}$
	TL 36 3119 (1995)	



Review: Chem Rev 95 2457 (1995)

R^1X $ArBr(I)$

CC 866 (1979)

Pure Appl Chem 57 1749 (1985)

TL 27 3745 (1986); 32 43 (1991); 33 6919 (1992);

35 27 (1994); 36 1679 (1995)

SL 25 (1989)

JOC 57 6995 (1992); 59 6095, 6501, 7164 (1994)

 $ArCl \cdot Cr(CO)_3$

TL 34 107 (1993)

 $ArOTf$

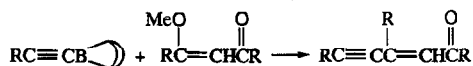
SL 221 (1990)

JOC 53 2001 (1993); 58 2201 (1993)

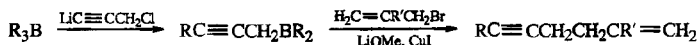
 $RC \equiv CBr$

Pure Appl Chem 57 1749 (1985)

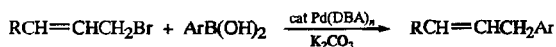
TL 35 27 (1994)



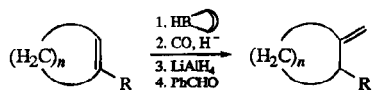
JOC 42 3106 (1977)



CL 1289 (1982)



JOC 60 2396 (1995)

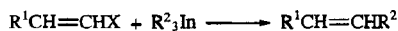


JOC 46 647 (1981)

4. Aluminum Reagents

See page 379, Section 13; page 382, Section 20; page 386, Section 21; and page 590, Section 3.

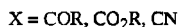
5. Indium Reagents



$X = Cl, Br, R^2 = 1^\circ, 2^\circ \text{ alkyl}$

JACS 114 2738 (1992)

6. Thallium Reagents



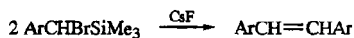
JOMC 99 C8 (1975)

BCSJ 53 553 (1980)

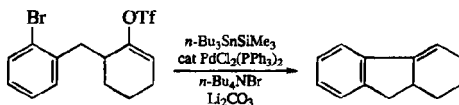
JOC 51 3708 (1986)

7. Silicon Reagents

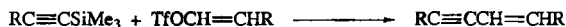
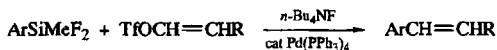
For other reactions of allylic silanes, look under the functional group introduced; see also page 386, Section 21 and page 591, Section 5.



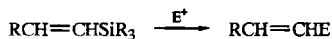
JOC 56 3908 (1991)



JOC 56 3486 (1991)

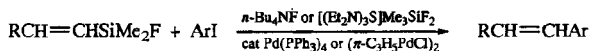


TL 31 2719 (1990)

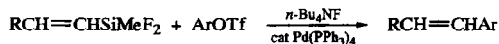


Org Rxs 37 57 (1989) (review)

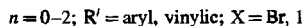
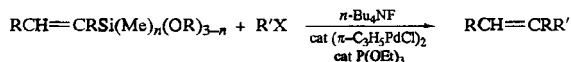
See appropriate sections based on the electrophile employed.



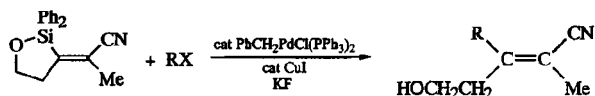
JOC 54 268 (1989)



TL 31 2719 (1990)

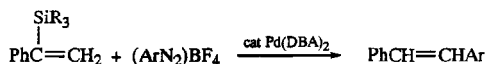


TL 30 6051 (1989)



$\text{RX} = \text{ArCH}_2\text{Br, ArI}$

TL 35 8637 (1994)



CL 873 (1988)



X

Reagent(s)

H

$\text{H}_2\text{CO, H}^+$

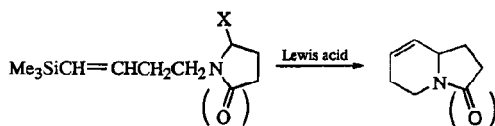
CH_2SiMe_3

$(n\text{-Bu}_4\text{N})_2\text{Ce(NO}_3)_6$

CH_2CN

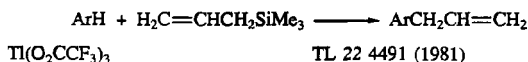
AgBF_4

TL 34 5243 (1993)



$\text{X} = \text{OAc, SEt}$

JOC 54 2591 (1989)

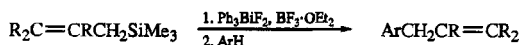


$\text{Ti(O}_2\text{CCF}_3)_3$

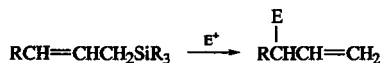
TL 22 4491 (1981)

$\text{PhTi(O}_2\text{CCF}_3)_2$

Chem Pharm Bull 30 3994 (1982)



TL 36 7475 (1995)



Reviews:

Pure Appl Chem 55 1707 (1983) (stereochemistry)

Org Rxs 37 57 (1989)

E^+ $R_3CCl, TiCl_4$

TL 4925 (1978); 33 4479 (1992)

Syn 446 (1979)

JOC 45 3559 (1980)

JACS 104 4962 (1982)

 R_3CX ($X = OTf, OSiMe_3, OAc$), Lewis acid

JOC 47 3219 (1982)

 R_fI , cat $Fe_3(CO)_{12}$ or $Ru_3(CO)_{12}$

TL 25 307 (1984)

 $PhIO, BF_3 \cdot OEt_2 / ArH$ ($E = Ar$)

TL 29 667 (1988)

 $Ar_2C(Me)Cl$, Lewis acid

JACS 113 4954 (1991)

 RX ($R =$ allylic, benzylic; $X =$ halogen, OR), $TiCl_4$

TL 23 2953 (1982)

 $ArCH_2SiMe_3, VO(OEt)Cl_2$ ($E = CH_2Ar$)

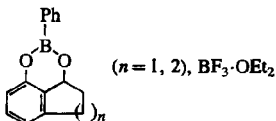
TL 35 8005 (1994)

 $ArCR_2OH, BF_3 \cdot OEt_2$

JOC 47 2125 (1982)

 $ArCHROH, SnCl_4$

TL 32 2087 (1991)



TL 35 3691 (1994)

 $(OC)_3Cr \cdot ArCR_2OAc, BF_3 \cdot OEt_2$

TL 31 2319 (1990)

JACS 113 5402 (1991)

 Ar_2CHOTf

TL 34 3393 (1993)

 RNO_2 ($R =$ allylic, benzylic), $SnCl_4$

CC 1285 (1986)

 $ArCH_2SO_2Ph, EtAlCl_2$

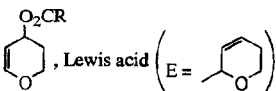
TL 33 4595 (1992)

 p -quinone methide (intramolecular $E = CH_2Ar$)

JACS 111 1136 (1989)

 $R_2C=CRCH_2OH(OAc), LiClO_4$

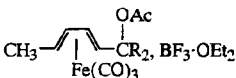
JOC 57 2986 (1992)



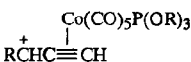
JOC 47 3803 (1982)

TL 28 4951 (1987); 30 6271 (1989)

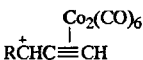
JACS 109 2082, 8117 (1987); 110 4368 (1988); 111 2967 (1989)



TL 28 641 (1987)



See page 594, Section 8.



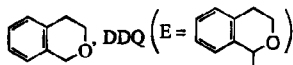
See page 594, Section 8.

epoxides, Lewis acid

See page 1045, Section 4.1.



JOC 50 2782 (1985)

E^+ 

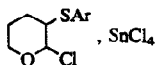
TL 34 8189 (1993)



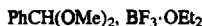
CL 409 (1983)



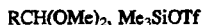
JOC 48 1557 (1983)



TL 34 3047 (1993)



JOC 48 3351 (1983)



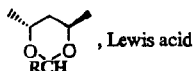
TL 29 3247 (1988) (intramolecular)

JACS 113 6594 (1991)

JOC 58 579 (1993)

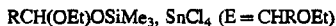


TL 34 7335 (1993)

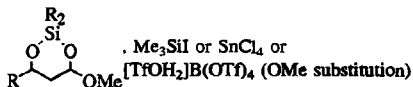


JACS 104 7371 (1982); 105 2088 (1983); 113 8089 (1991)

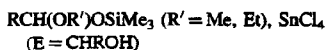
TL 25 3951 (1984)



JOC 60 2153 (1995)



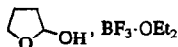
JACS 114 2745 (1992)



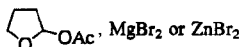
JOC 60 2153 (1995)



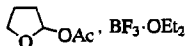
JOC 60 6141 (1995)



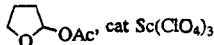
See page 951, Section 3.



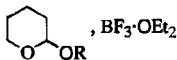
JOC 54 4100 (1989)



JOC 54 4100 (1989)

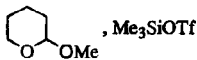


TL 35 3319 (1994)

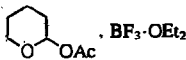


JOC 52 2335 (1987)





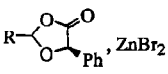
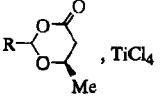
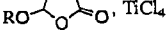
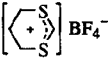

TL 30 407 (1989)

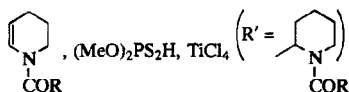


JOC 52 892 (1987)

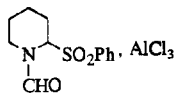


JOC 54 2034 (1989)

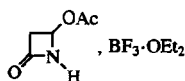
- 
, $(\text{Ph}_3\text{C})\text{ClO}_4$ TL 31 3813 (1990)
- 
, Me_3SiOTf TL 34 7541 (1993)
- 
, Lewis acid TL 24 1563 (1983)
JOC 50 3017 (1985)
- 
, $\text{BF}_3 \cdot \text{OEt}_2$ CC 1245 (1987)
- 
, ZnBr_2 JOC 49 2513 (1984)
- 
, TiCl_4 Angew Int 25 178 (1986)
- 
, TiCl_4 TL 36 7315 (1995) (intramolecular)
- $n\text{-Bu}_3\text{SnCHROCO}_2\text{Me}$, electrolysis TL 35 5247 (1994)
(E = CHROCO_2Me)
- PhSCH_2Cl , TiCl_4 TL 23 723 (1982)
CL 961 (1982)
- PhSCHClR , Lewis acid TL 24 1711 (1983)
- PhSCHROAc , electrolysis (E = CHRSPH) JOC 57 2946 (1992)
- $\text{RCH}(\text{SAr})_2$, SnCl_4 JACS 109 7199 (1987)
JOC 55 5966 (1990)
- $\text{PhSCH}(\text{NO}_2)\text{R}$, SnCl_4 CC 947 (1987)
- PhSCHRCHRNO_2 , AlCl_3 or TiCl_4 JOC 52 4133 (1987); 54 4998 (1989)
(E = PhSCHRCHR)
- $\text{PhX}-\text{C}-\text{C}-\text{Cl}$ (X = S, Se), ZnBr_2 TL 24 5911 (1983)
- 
 BF_4^- TL 23 4835 (1982)
- $\text{R}_2\text{C}(\text{SeMe})_2$, SnCl_4 TL 31 4363 (1990)
- $\text{RCH}=\text{NR}$, SnCl_4 See page 847, Section 3.
- $\text{RCONHCHRO-}i\text{-Pr}$, HCO_2H (E = RCONHCHR) JOC 59 3530 (1994)
- $\text{RCON}(\text{Me})\text{OTf}$ (E = RCONHCH_2) JOC 59 3530 (1994)
TL 35 3231 (1994)
- $\text{RCONHCH}_2\text{N}$

, $\text{BF}_3 \cdot \text{OEt}_2$ (E = RCONHCH_2) JOC 60 4002 (1996)

E^+ 

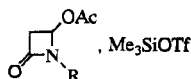
SL 797 (1991)



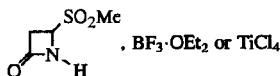
SL 48 (1990)



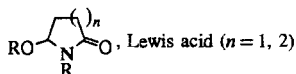
CC 134 (1982)



TL 36 4283 (1995) (intramolecular)



SL 885 (1991)

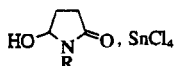


CC 134 (1982)

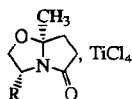
JOC 55 215 (1990); 57 6360 (1992); 60 6114 (1995)

JACS 112 2003 (1990)

TL 31 4949 (1990); 35 6119 (1994)



JOC 55 4688 (1990); 56 4868 (1991)



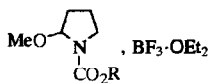
JACS 113 9858 (1991)

TL 35 2223 (1994)

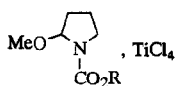


CC 134 (1982)

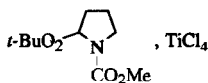
TL 34 6131 (1993)



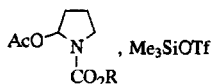
JOC 55 1406 (1990)



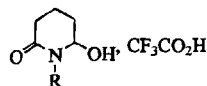
JOC 56 2787 (1991)



JACS 112 7820 (1990)



JOC 56 2787 (1991)



TL 33 73 (1992) (intramolecular)

$\text{Me}_3\text{SiOC}(\text{Me})(\text{NHCHO})\text{CO}_2\text{Me}$, Me_3SiOTf
 $[\text{E} = \text{C}(\text{Me})(\text{NHCHO})\text{CO}_2\text{Me}]$

SL 451 (1992)

JOC 58 3259 (1993)

$\text{AcOCR}(\text{NHCOMe})\text{CO}_2\text{Et}$, $\text{BF}_3 \cdot \text{OEt}_2$
 $[\text{E} = \text{CR}(\text{NHCOMe})\text{CO}_2\text{Et}]$

JOC 58 3259 (1993)

$\text{MeOCH}(\text{NHCO}_2\text{R})\text{CONR}_2$, HCO_2H or $\text{BF}_3 \cdot \text{OEt}_2$
 $[\text{E} = \text{CH}(\text{NHCO}_2\text{R})\text{CONR}_2]$

JOC 57 6769 (1992)

$\text{ClCH}(\text{NHCO}_2\text{Me})\text{CO}_2\text{Me}$, SnCl_4
 $[\text{E} = \text{CH}(\text{NHCO}_2\text{Me})\text{CO}_2\text{Me}]$

Tetr 45 4627 (1989)

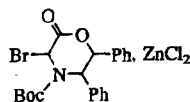
$\text{MeOCR}(\text{NHCO}_2\text{Me})\text{CO}_2\text{Me}$, $\text{BF}_3 \cdot \text{OEt}_2$
 $[\text{E} = \text{CR}(\text{NHCO}_2\text{Me})\text{CO}_2\text{Me}]$

Tetr 45 4627 (1989)

JOC 58 3259 (1993)

$\text{AcOCH}(\text{NRCO}_2\text{Me})\text{CO}_2\text{Me}$, EtAlCl_2
 (intramolecular) $[\text{E} = \text{CH}(\text{NRCO}_2\text{Me})\text{CO}_2\text{Me}]$

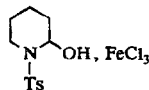
SL 38 (1989)



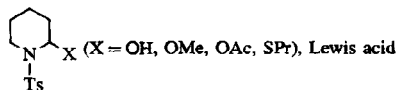
JACS 110 1547 (1988)

 $\text{RCH}(\text{OMe})\text{NHTs}$, TiCl_4

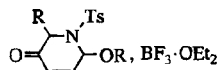
JACS 112 2368 (1990)



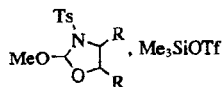
JOC 58 4945 (1993) (intramolecular)



SL 1149 (1995)



TL 36 4315 (1995)



SL 99 (1990)

 dienone , TiCl_4 (1,6-addition)

TL 29 1533 (1988)

 ClSO_2NCO ($\text{E} = \text{CN}$)

TL 32 1583 (1991)

 PhSCl ($\text{E} = \text{SPh}$)

TL 32 1583 (1991)

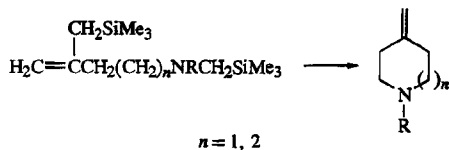
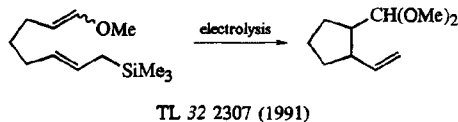
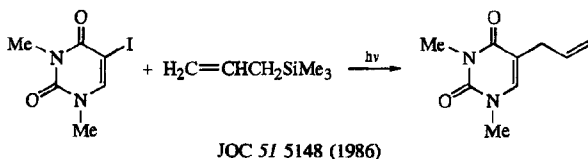
 $\text{NsONHCO}_2\text{R}$, Et_3N ($\text{E} = \text{NHCO}_2\text{R}$)

TL 34 4101 (1993)

 $(\text{NO}_2)\text{BF}_4$

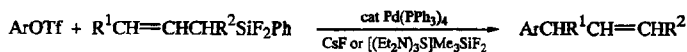
JOC 60 7714 (1995)

For $\text{R}' = \text{OH}$, see page 234, Section 6.

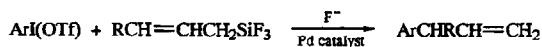


Reagent: photolysis, electrolysis, $(n\text{-Bu}_4\text{N})_2\text{Ce}(\text{NO}_3)_6$, $\text{Pb}(\text{OAc})_4$ or $\text{Mn}(\text{OAc})_3$

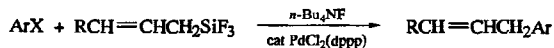
TL 34 5239 (1993)



TL 35 1279 (1994)

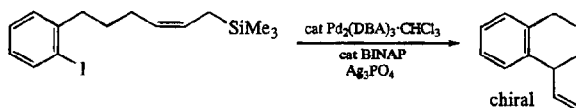


JACS 113 7075 (1991)

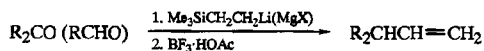


$\text{X} = \text{Br}, \text{I}, \text{OTf}$

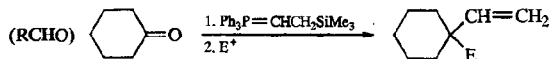
TL 35 6511 (1994)



Angew Int 33 1089 (1994)
SL 597 (1995)



JOC 47 1983 (1982)



$\text{E}^+ = \text{BF}_3 \cdot \text{HOAc}$ ($\text{E} = \text{H}$), RX-TiCl_4 , RCOCl-TiCl_4 , enone- TiCl_4 , epoxide- TiCl_4

Syn 446 (1979)

8. Germanium Reagents

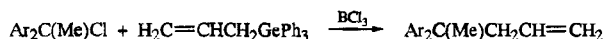


$\text{Ti}(\text{O}_2\text{CCF}_3)_3$

TL 22 4491 (1981)

$\text{PhTi}(\text{O}_2\text{CCF}_3)_2$

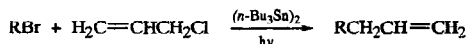
Chem Pharm Bull 30 3994 (1982)



JACS 113 4954 (1991)

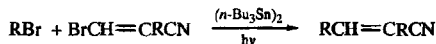
9. Tin Reagents

For other reactions of allylic stannanes, look under the functional group introduced; see also page 386, Section 21.

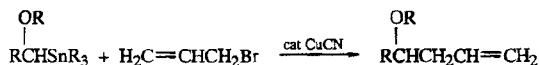


$\text{R} = 1^\circ, 2^\circ, 3^\circ \text{ alkyl}$

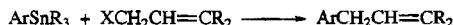
TL 34 3041 (1993)



TL 34 3041 (1993)



JACS 117 5973 (1995)



X

Catalyst

Cl, Br

Pd(O)

JACS 105 7173 (1983); 106 4833 (1984);
112 2813, 8188, 8612 (1990); 113 5775
(1991)

TL 28 1191 (1987); 36 6507 (1995)

JOC 55 5833 (1990); 59 4250 (1994)

Br

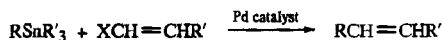
ZnCl_2

TL 24 1905 (1983)

OAc

Pd(DBA)_2 , LiCl

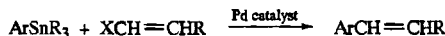
JOC 55 3019 (1990)



R = alkyl

X

halogen	TL 30 3645 (1989); 32 3391, 4397 (1991) SL 53, 157 (1991) JACS 114 6556 (1992)
OTf	JACS 106 4630 (1984); 108 3033 (1986) JOC 54 5828 (1989); 55 5833 (1990); 60 7821 (1995) TL 35 2509 (1994)

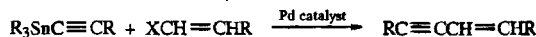


X

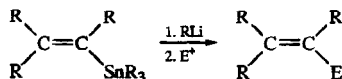
halogen	Proc Acad Sci USSR, Chem Sec 272 333 (1983) JOC 54 4734 (1989); 55 6184 (1990); 58 7870 (1993); 59 4250 (1994); 60 6218 (1995) TL 31 4293 (1990); 32 3391, 4397 (1991); 33 919 (1992); 35 2081, 2405 (1994); 36 2191, 3111, 6507, 7225 (1995) SL 573, 771 (1993)
OSO ₂ F	TL 32 4073 (1991)
OTf	TL 29 6043 (1988); 31 1347, 2853 (1990); 32 4243 (1991); 35 2405, 2509 (1994); 36 2191, 3099 (1995) JOC 55 5833 (1990); 58 5434 (1993); 59 4250 (1994); 60 7821 (1995)



SL 1047 (1994)



See page 592, Section 6.

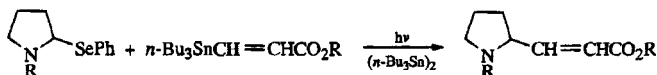


E⁺ = RX, RCHO, R₂CO, ClCO₂R, Me₃SiCl, R₃SnCl, RSSR

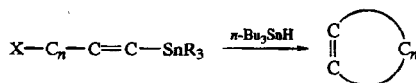
- CC 926 (1986)
JOC 54 4721 (1989)
JACS 113 3096 (1991)
TL 32 3329, 4121 (1991); 33 5841 (1992) (intramolecular); 35 3797 (1994); 36 389 (1995)

RX

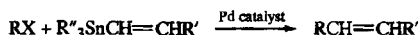
- 1°, 2°, 3° RBr CC 682 (1985)
 2° RBr CC 133 (1984)
 1°, 2° RBr, ArBr(I) JOC 53 1127 (1988)
 1° RI TL 28 2941 (1987) (intramolecular); 29 4865 (1988);
 34 2715 (1993)
 JOC 59 4048 (1994)
 1°, 2° RI JCS Perkin I 1689 (1994)
 2° ROC(S)OAr JOC 53 1127 (1988)
 SL 677 (1993)
 TL 35 4697, 5225 (1994)



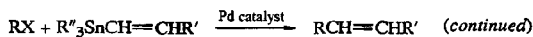
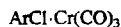
JOC 55 5194 (1990); 56 2787 (1991)



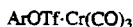
JACS 112 5601 (1990)

RX

- R_fI TL 28 5857 (1987)
 ArCH₂Br JACS 112 4078 (1990); 114 3910, 3926 (1992)
 SL 444 (1992)
 JOC 58 165 (1993); 59 4735 (1994)
 TL 33 4885 (1992)
 ROCH₂X (X = Cl, Br) TL 33 4885 (1992)
 ArX Proc Acad Sci USSR, Chem Sec 272 333 (1983)
 Macromolecules 18 321 (1985)
 JOC 52 422 (1987); 53 1170, 3051 (1988); 54 4721
 (1989); 55 2572, 3114, 5359, 5808 (1990); 56
 2883, 5459 (both intramolecular), 6379 (1991); 57
 565 (1992); 58 1443 (1993); 59 4143, 4346, 5414,
 5905, 7164, 7553, 7917 (1994); 60 2378, 6608
 (1995)
 JACS 109 7223 (1987); 111 8502 (1989) (hetero-
 cycle); 112 7399, 7410 (1990); 113 9585 (1991);
 116 5540 (1994); 117 211 (1995)
 TL 29 2783 (1988); 31 1837, 1857, 5165, 6077
 (1990); 32 4121, 4341 (1991); 32 409, 413 (1992);
 33 7049 (1992); 34 1571, 6211, 8353 (1993); 35
 1027, 3155, 5177, 5613, 6551 (1994); 36 775,
 1945, 3111, 5319, 5969, 7043 (1995)
 SL 32, 957 (1995)

RXCC 1755 (1987)
TL 34 107 (1993)

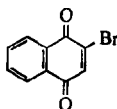
JOC 57 6321 (1992)

JACS 109 5478 (1987); 113 9585 (1991)
JOC 53 1170 (1988); 55 906, 3114 (1990); 56 2883
(1991) (intramolecular); 57 678 (1992); 59 5905
(1994); 60 6608 (1995)
TL 31 1837, 2357, 5189 (1990); 34 6211 (1993); 35
5047, 5177 (1994); 36 421 (1995)
SL 709 (1991); 32 (1995)

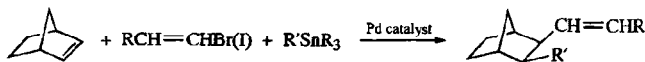
JACS 116 7449 (1994)



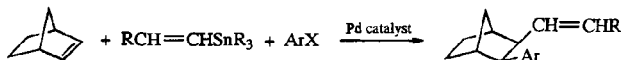
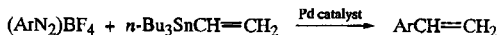
JOC 56 3493 (1991)



JOC 59 6075 (1994)

JOC 55 5359 (1990); 59 3755 (1994)
TL 33 3647 (1992)
SL 463 (1993)
JACS 116 5050 (1994)

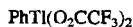
R' = aryl, vinylic, alkynyl

Tetr 45 961 (1989)
BCSJ 66 3522 (1993)Tetr 45 961 (1989)
BCSJ 66 3522 (1993)

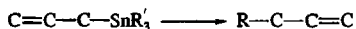
JOC 48 1333 (1983)



TL 22 4491 (1981)



Chem Pharm Bull 30 3994 (1982)



MeOTf, MABR

JACS 114 4422 (1992)

RX [R = 1°, 2°, 3° alkyl; allylic; benzylic; X = Cl, Br, I, OC(S)OPh, SPh, SePh], free radical initiation or hv

JOMC 26 C4 (1971); 56 C11 (1973); 61 C33 (1973); 96 225 (1975)

JACS 104 5829 (1982); 112 6738 (1990)

JOC 47 3590 (1982); 49 1462 (1984); 52 3659

(1987); 55 4699, 6236 (1990); 57 4457 (1992); 58 3840 (1993); 59 6153 (1994)

TL 24 1357 (1983); 25 1867 (1984); 26 3311 (1985) (intramolecular); 27 4857 (1986); 29 4865, 6969 (1988); 31 597, 1467, 2983, 5693 (1990); 32 27, 3953, 6097 (1991); 33 6931 (1992); 34 1741, 5491 (1991)

BCSJ 56 2480 (1983)

Tetr 41 4079 (1985)

CC 1339 (1986)

SL 677, 871 (1993); 449 (1995)

RX (X = Br, I), ZnCl₂

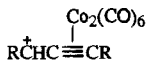
JACS 116 421 (1994)

Ar₂C(Me)Cl, BCl₃ or Me₃SiOTf

JACS 113 4954 (1991)

Ar₂CHOTf

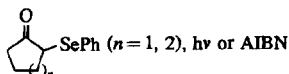
TL 34 3393 (1993)



See page 594, Section 8.

R₇I, cat Pd(PPh₃)₄

TL 28 5857 (1987)



JOC 55 1277 (1990)

PhSeCHRCOX (X = alkyl, OR), hv

JACS 110 4815 (1988)

RCOCH₂X, AIBN (R = RCOCH₂)

CL 795 (1978)

R₂NCOCHIR

JACS 114 7007, 7664 (1992)

RCONRCOCHIR

JACS 114 7007 (1992)

RO₂CCHBrNRCOR

TL 29 1565 (1988)

RO₂CCHBrNHCOR

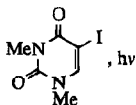
JOC 55 384 (1990)

NO₂CRFCO₂R (R = CRFCO₂R)

JOC 58 3483 (1993)

NO₂CR₂F (R = CR₂F)

JOC 58 3483 (1993)



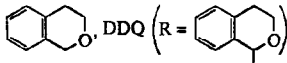





JOC 51 5148 (1986)

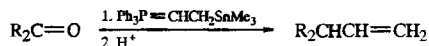
ArX, Pd catalyst (R = Ar)

CL 301 (1977)

TL 28 3935 (1987); 29 5739 (1988)

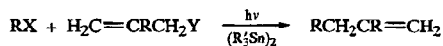
JOC 59 5905 (1994); 60 1856, 4647 (1995)

- ArOTf, Pd catalyst (R = Ar) JACS 109 5478 (1987); 113 9585 (1991)
 TL 31 2357 (1990)
 JOC 55 906 (1990); 57 678 (1992); 59 6567 (1994);
 60 4647 (1995)
- Het-Br, Pd catalyst SL 1227 (1995)
- RCH(OR)₂ or R₂C(OR)₂, Lewis acid See page 931, Section 1.
- RCH(OR)OAlR₂, TiCl₂(O-*i*-Pr)₂ TL 34 5729 (1993)
- RCH(OR)OAlR₂, ZnBr₂ TL 34 5777 (1993)
- RCH(OMe)SeMe, Lewis acid (R = CHROME) JOC 60 6141 (1995)
- , DDQ (R = ) TL 34 8189 (1993)
- PhS , *n*-Bu₃SnOTf TL 35 5841 (1994)
- RCH(O₂CR)SePh, AIBN TL 35 9721 (1994)
- R₂C(SMe)₂, (Me₂SSMe)BF₄ (R = CR₂SMe) JACS 107 719 (1985)
- RCH=NR, Lewis acid See page 847, Section 3.
- immonium salts (R = CH₂NR₂) JOC 52 1378 (1987)
- X  (X = OH : MsCl, Et₃N; X = SPh : hv) JOC 54 4345 (1989) (intramolecular)
- RO , MgBr₂ TL 31 4949 (1990)
- AcO , MgBr₂ JOC 60 103 (1995)
- dienone, AlCl₃ (1,6-addition) TL 29 1533 (1988)



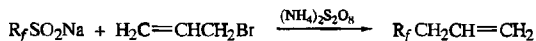
CC 630 (1975)

10. Sulfur Reagents

X = Br, I, SePh; Y = SPh, SSi(SiMe₃)₃

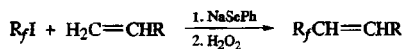
JOC 50 5442 (1985)

TL 33 6931 (1992)

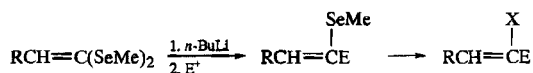


JOC 56 2801 (1991)

11. Selenium Reagents

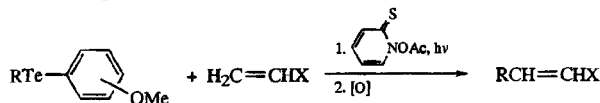


TL 32 375 (1991)

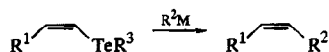
E⁺ = H₂O, D₂O, MeI, RCHO, R₂CO, Me₂NCHO, ClCO₂Me, CO₂X = H (*n*-Bu₃SnH), Br (Br₂)

TL 23 3411 (1982)

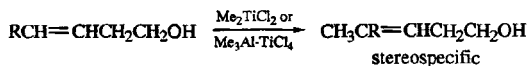
12. Tellurium Reagents

X = COR, CO₂R, CONR₂, SO₂R

JACS 112 891 (1990)

R²MR²Cu(CN)Li SL 671 (1995)R²₂Cu(CN)(MgX)₂ TL 35 4063 (1994)ThCu(R²)(CN)(Li)MgX SL 671 (1995)R²Cu(CN)MgX SL 671 (1995)

13. Titanium Reagents



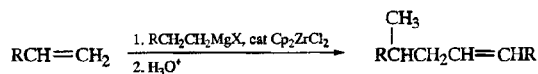
CL 1819 (1982)

Angew Int 21 309 (1982)

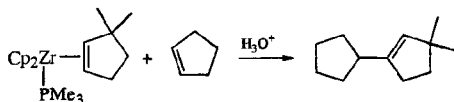
TL 26 4423 (1985)

14. Zirconium Reagents

See also page 382, Section 20.

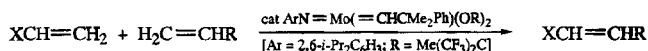


TL 33 1965 (1992)



JACS 111 9113 (1989)

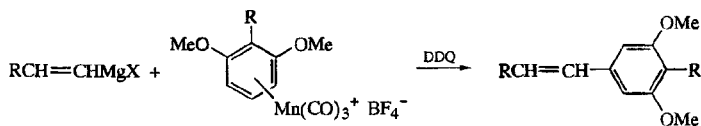
15. Molybdenum Reagents



JACS 115 10998 (1993) (X = Ar); 117 5162 (1995) (X = CN)

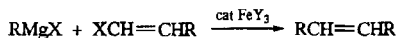
See page 559, Section 8 for olefin metathesis leading to cycloalkenes.

16. Manganese Reagents



JOC 57 4040 (1992)

17. Iron Reagents

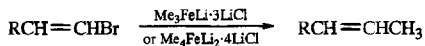


X = halogen

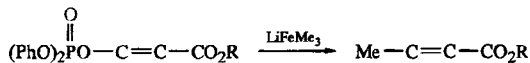
JACS 93 1487 (1971) (Y = Cl)

Syn 303 (1971) (Y = Cl)

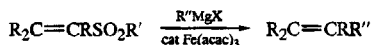
JOC 40 599 (1975); 41 502 (1976) (both Y = PhCOCHCOPh)

JOMC 312 343 (1986) (Y = RCOCHCOR, R = *t*-Bu, Ph)

TL 31 507 (1990)

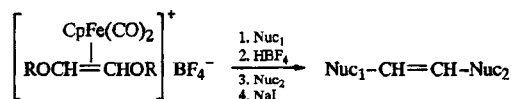


TL 27 905 (1986)



$R' = t\text{-Bu, Ph; } R'' = 1^\circ \text{ alkyl, Ph}$

TL 23 2469 (1982)



$\text{Nuc}_1, \text{Nuc}_2 = R_2\text{CuLi, } R_2\text{CuLi; } R_2\text{CuLi, ketone enolate; } R_2\text{CuLi, PhMgBr; } R_2\text{Cu(CN)Li}_2, R_2\text{Cu(CN)Li}_2; R_2\text{Cu(CN)Li}_2, \text{PhMgBr}$

JACS 106 7264 (1984)



$R = 1^\circ, 2^\circ \text{ alkyl; benzylic; aryl; vinylic; alkynyl}$

SL 513 (1991)

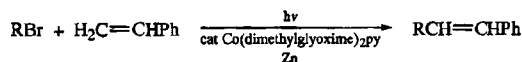
18. Ruthenium Reagents



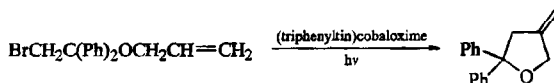
$X = \text{COR, CO}_2\text{R, CONHR}$

JACS 117 5371 (1995)

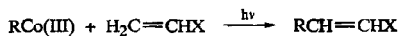
19. Cobalt Reagents



TL 32 6273 (1991)



JOC 60 6635 (1995)

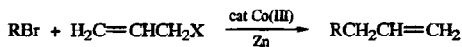


R = 1°, 2° alkyl; X = Ph, COR, CO₂R, CN

CC 871 (1987)

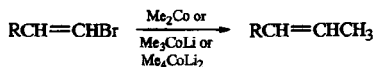
TL 29 167, 3191 (1988)

JOC 54 1320 (1989)



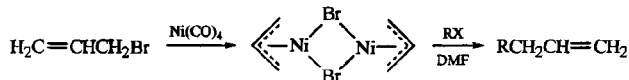
X = SPh, SO₂Ph, SePh, OPO(OPh)₂

TL 33 4545 (1992)



TL 31 511 (1990)

20. Nickel Reagents



R = alkyl, aryl, vinylic

Reviews:

Org Rxs 19 115 (1972)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 2.1, p 413

JACS 89 2755 (1967); 97 459 (1975); 100 5800 (1978); 107 5574, 5663 (mechanism) (1985)

CC 235, 2289 (1973)

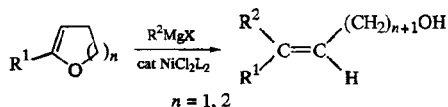
BCSJ 47 3098 (1974); 49 3351 (1976)

JCS Perkin I 2411 (1981)

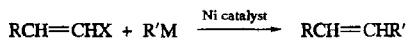
Organomet 1 259 (1982)

Org Syn Coll Vol 6 722 (1988)

JOC 54 4141 (1989); 58 997 (1993)



See page 1061, Section 4.3.



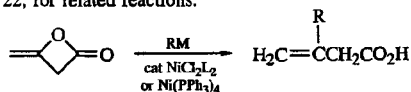
<u>X</u>	<u>R'M</u>	
halogen	$\text{RO}_2\text{CCH}_2\text{Li}$	See page 1724, Section 2.
	RMgX (review)	Pure Appl Chem 52 669 (1980)
	RMgX ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl)	JACS 94 4374 (1972); 104 180 (1982)
		JOMC 55 C91 (1973); 168 227 (1979); 312 343 (1986)
		Helv 56 460 (1973)
		TL 3 (1974); 22 137, 315 (1981); 24 3209 (1983); 28 6351 (1987); 34 2509 (1993); 35 2067 (1994)
		BCSJ 49 1958 (1976)
		CL 767 (1980)
		CC 647 (1982)
		JOC 48 2195 (1983); 50 3261 (1985); 52 678 (1987)
	$\text{Me}_3\text{SiCH}_2\text{MgCl}$	Org Syn Coll Vol 6 407 (1988)
		TL 23 27 (1982); 28 6351 (1987); 34 2509 (1993)
	RMgX ($\text{R} = \text{benzylic}$)	Helv 56 460 (1973)
		TL 3 (1974); 21 79, 4623 (1980); 27 2049 (1986)
		JACS 98 3718 (1976); 104 180 (1982)
		BCSJ 49 1958 (1976)
		JOMC 209 C1 (1981)
		CC 647 (1982); 1746 (1987)
		JOC 48 2195 (1983); 50 3261 (1985); 51 5169 (1986)
		Org Syn Coll Vol 6 407 (1988)
	RMgX ($\text{R} = \text{vinyl}$)	See page 476, Section 3.2.
	ArMgX	JACS 94 4374 (1972)
		CC 144 (1972); 647 (1982); 883 (1986)
		JOMC 55 C91 (1973); 168 227 (1979)
		BCSJ 49 1958 (1976)
		JOC 52 678 (1987); 57 1784 (1992)
		TL 28 6351 (1987); 34 2509 (1993)
		Org Syn Coll Vol 6 407 (1988)
		See page 585, Section 1.
		Bull Acad Sci USSR, Div Chem Sci 620 (1986)
	$\text{RC}\equiv\text{CMgX}$	See page 1724, Section 2.
	RZnX ($\text{R} = 1^\circ$ alkyl)	TL 21 3915 (1980)
	$\text{EtO}_2\text{CCH}_2\text{ZnBr}$	
	OSiMe_3	RMgX ($\text{R} = 1^\circ$ alkyl, aryl, benzylic)
	$\text{OPO}(\text{OEt})_2$	$\text{Me}_3\text{SiCHRMgCl}$
	OCONR_2	RMgX ($\text{R} = \text{Me}, n\text{-Bu}, \text{Ph}, \text{Me}_3\text{SiCH}_2$)
	OR	RMgX ($\text{R} = \text{Ph}, 1^\circ$ alkyl)
		JACS 101 2246 (1979)
		JOC 49 4894 (1984); 50 719 (1985)
		CC 241, 429 (1987)

<u>X</u>	<u>R'M</u>	
SR	RMgX (R = 1° alkyl, aryl)	TL 43 (1979); 25 5177 (1984); 27 6301 (1986); 30 243 (1989) CC 637 (1979); 647, 840 (1982) CL 1209 (1980) JACS 114 10674 (1992) JACS 114 10674 (1992)
	Ph ₂ Zn·MgBr ₂	JACS 110 4062 (1988)
SOR	MeMgBr	JACS 111 1125 (1989)
SO(Ph)NMe	R ₂ Zn, MgBr ₂ (R = 1° alkyl, aryl)	TL 23 2469 (1982); 35 5369 (1994)
SO ₂ R	RMgX (R = Me, Ph)	TL 35 6729 (1994)
SeMe	Me ₃ SiCH ₂ MgCl	TL 21 87 (1980)
SePh	RMgX (R = n-Bu, Ph)	



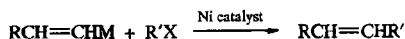
<u>X</u>	<u>R'M</u>	
R	R ₃ Al, cat Ni(acac) ₂	Chem Ind 606 (1981)
OR	Me ₃ SiCH ₂ MgCl, cat Ni(acac) ₂	Can J Chem 60 673 (1982) TL 28 2753 (1987)
	Me ₂ Zn, cat Ni(acac) ₂	JACS 109 1564 (1987) (2-alken-4-olide)

See also page 392, Section 22, for related reactions.

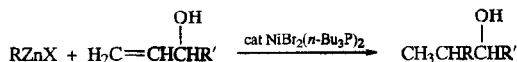


RM = 1° RMgBr, RCH=CHAl(*i*-Bu)₂, RC≡CZnCl, ArZnCl

Chem Pharm Bull 31 1108, 4346 (1983)

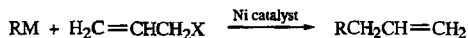


<u>M</u>	<u>R'X</u>	
MgX	ArX	BCSJ 49 1958 (1976) JOC 50 5370 (1985)
Al(<i>i</i> -Bu) ₂	ArX	CC 596 (1976) JACS 109 2393 (1987) TL 22 4449 (1981)
	ArOPO(OEt) ₂	JACS 103 4466 (1981); 109 2393 (1987)
ZrClCp ₂	ArX	

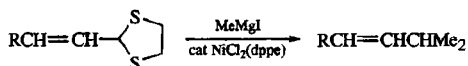


R = benzylic, allylic

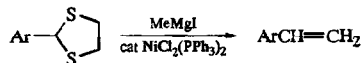
TL 30 6409 (1989)



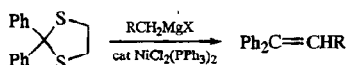
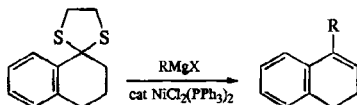
<u>X</u>	<u>RM</u>	
Cl	MeZnCl (<i>i</i> -PrO ₂ CCH ₂ CH ₂) ₂ Zn	TL 29 5155 (1988) See page 1724, Section 2.
Cl, OR, OSiR ₃	PhMgBr	CC 313 (1981)
Br, OH, OPh, S- <i>t</i> -Bu	RMgX (R = Me, Et)	Tetr 42 2043 (1986)
OH	RMgX (R = 1° alkyl, benzylic, aryl)	JOMC 127 371 (1977); 134 265 (1977) Helv 63 987 (1980) CC 313, 681 (chiral) (1981) TL 28 4547 (1987)
OPh	RMgBr (R = Et, Ph)	CC 112 (1983)
OTHP	PhMgX	TL 29 3373 (1988)



JOC 54 2262 (1989); 56 5289 (1991)



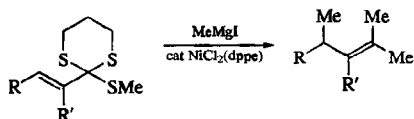
JOC 56 4035 (1991)



CC 1515 (1987)

JOC 56 4035 (1991)

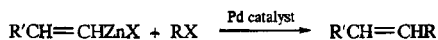
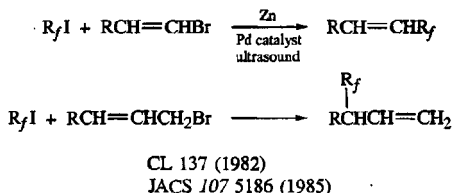
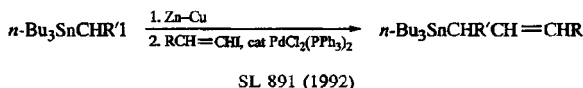
JACS 114 7308 (1992); 116 8920 (1994)



JOC 56 5289 (1991)

21. Palladium Reagents

See also page 362, Section 3; page 365, Section 6; page 365, Section 7; page 373, Section 9; and page 400, Section 25.



RX

ArCH₂Br

JOC 60 290 (1995)

ArI(Br)

JOC 53 2714 (1988); 54 4727 (1989); 56 7336 (1991); 58 1167 (1993); 60 290 (1995)

TL 31 4393 (1990); 33 6139 (1992); 34 107, 5333 (1993)

JACS 112 8188 (1990)

SL 886 (1992); 279 (1993); 516 (1995)

ArOTf

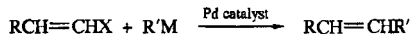
SL 886 (1992)

RCH=CHI

See page 514, Section 3.24.

RC≡Cl

See page 596, Section 10.



X

halogen

R'M

RLi (R = 1° alkyl, aryl)

JOMC 91 C39 (1975)

JOC 44 2408 (1979)

Org Syn 62 39 (1984)

Org Syn Coll Vol 7 172 (1990)

RMgX (R = 1°, 2° alkyl)

JOMC 91 C39 (1975); 312 343 (1986)

TL 191 (1978); 1073, 1871 (1979); 27

2529 (1986); 30 403 (1989)



JOC 44 2408 (1979); 48 2195 (1983);

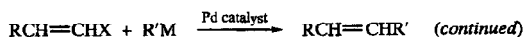
51 3772 (1986); 58 6779 (1993)

CC 647 (1982)

JACS 104 180 (1982); 106 158 (1984)

SL 665 (1994)

$\text{Me}_3\text{SiCH}_2\text{MgCl}$	TL 23 27 (1982) SL 665 (1994)
RMgX (R = benzylic)	CC 647 (1982); 1746 (1987) JOC 51 3772 (1986) TL 36 3745 (1995) (chiral)
ArMgX	TL 191 (1978) CC 647 (1982) JACS 109 1257 (1987) JOC 55 6184 (1990); 58 4823 (1993) SL 665 (1994)
RMgX (R = vinylic)	See page 476, Section 3.2.
$\text{RC}\equiv\text{CMgX}$	See page 585, Section 1.
$\text{R}_3\text{SnR}'_3$ (R = alkyl, aryl)	See page 373, Section 9.
$\text{RC}\equiv\text{CSnR}_3$	See page 592, Section 6.
RCu(CN)ZnI	SL 499 (1993)
RZnX (R = 1° alkyl)	JACS 102 3298 (1980); 109 1257 (1987); 111 3336 (1989) JOC 46 4093 (1981); 51 4080 (1986); 52 4885 (1987); 55 5406 (1990) TL 24 3823 (1983); 30 4913, 6401, 6555 (1989); 33 6839 (1992); 34 1437, 2111 (1993); 36 2469 (1995) JOMC 285 109 (1985) Bull Acad Sci USSR, Div Chem Sci 620 (1986) SL 524 (1994)
RZnX (R = 2° alkyl)	TL 32 1573 (1991) SL 524 (1994)
	TL 28 5075 (1987)
 ', cat Pd	TL 30 6039 (1989) JOC 58 2958 (1993)
$\text{EtO}_2\text{CCH}_2\text{ZnBr}$	See page 1724, Section 2.
$\text{EtO}_2\text{C(CH}_2)_n\text{ZnI}$ (n = 2, 3)	See page 1724, Section 2.
$(\text{RO}_2\text{CCH}_2\text{CH}_2)_2\text{Zn}$	See page 1724, Section 2.
ArCH_2ZnX	TL 22 2715 (1981) SL 524 (1994)
ArZnX	JOC 30 2121 (1985); 55 6184 (1990); 56 4052, 4821 (1991) J Med Chem 29 2053 (1986) TL 30 6555 (1989); 32 5919 (1991); 33 4495, 6839 (1992); 34 1437 (1993); 35 6913 (1994); 36 2469 (1995) JACS 114 3983 (1992) SL 524 (1994); 344 (1995) See page 596, Section 10.
$\text{RC}\equiv\text{CZnX}$	
$\text{Me}_3\text{SiCH}_2\text{MgCl}$	Syn 1001 (1981)
R_3Al	TL 21 2531 (1980); 22 1609 (1981) BCSJ 57 108 (1984)

XR'M

OTf

R'SnR₃ (R' = alkyl), LiCl
 EtO₂C(CH₂)_nZnI (n = 2, 3)
 (RO₂CCH₂CH₂)₂Zn
 ArZnX

See page 373, Section 9.
 See page 1724, Section 2.
 See page 1724, Section 2.
 TL 28 701 (1987); 31 6721 (1990); 32
 5919 (1991)
 JACS 112 7399 (1990)
 SL 47 (1990)

SO₂R

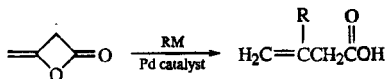
RMgX (R = Me, Ph)

TL 32 4583 (1991)

SeMe

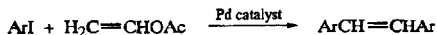
Me₂SiCH₂MgCl

TL 35 6729 (1994)

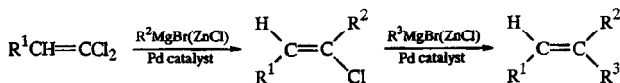


RM = RCH=CHAl(*i*-Bu)₂, RC≡CZnCl

Chem Pharm Bull 31 4346 (1983)

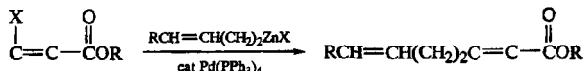


TL 31 1495 (1990)



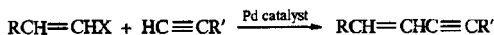
R¹, R² or R³ = aryl, 1° alkyl

JACS 109 1257 (1987)



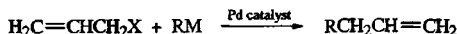
X = Cl, Br

JOC 45 5223 (1980) (also 3-halo-2-alken-4-olide)
 See also page 392, Section 22, for related reactions.



X = halogen, OTf

See page 596, Section 10.

XRM

Cl

BPh₄⁻

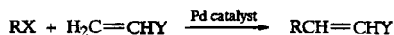
JACS 112 2813 (1990)

Br



Syn 51 (1987)

	$\text{NCCH}_2\text{CH}_2\text{ZnI}$	TL 29 2395 (1988)
Cl, Br	ArSnR'_3	See page 373, Section 9.
Cl, OR, OSiR ₃	RMgX	CC 313 (1981)
OH	RMgX	JOMC 186 C1 (1980) CC 313 (1981)
AcO	PhZnCl	TL 32 5091 (1991) (chiral)
RCO_2 (lactone)	PhZnCl	CC 160 (1982)
OTs	RZnX	JACS 114 4051 (1992)



R = aryl, heterocyclic, benzylic, vinylic

X = halogen, triflate

Y = H, CO_2R , CO_2H , CONH_2 , CN, Ar, alkyl, alkenyl, OR

Reviews:

Pure Appl Chem 50 691 (1978)

Acct Chem Res 12 146 (1979); 28 2 (1995)

J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980)

Org Rxs 27 345 (1982)

R. F. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985)

Chem Rev 89 1433 (1989)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Part 4.3, p 833

Angew Int 33 2379 (1994)

J. Tsuji, "Palladium Reagents and Catalysts: Innovations in Organic Synthesis," J. Wiley and Sons, New York (1995)

JOC 37 2320 (1972); 40 1083 (1975); 43 2454, 2941, 2947, 2949, 5018 (1978); 44 4078 (1979); 46 1067, 2767, 5414 (1981); 52 3319 (1987); 53 235, 2112 (1988); 54 249, 2507 (intramolecular), 4141 (intramolecular) (1989); 55 63, 906, 3654, 4175, 5757, 6028 (inter- and intramolecular) (1990); 56 1289, 2584, 5796 (1991); 57 3242, 3558, 4612 (1992); 58 3299, 4441, 4823 (intramolecular), 7388, 7421 (1993); 59 192, 355 (intramolecular), 4272, 4418 (intramolecular), 5358 (catalyst on polymer), 6142 (intramolecular), 6902, 7096 (1994); 60 1013 (intramolecular), 1486, 2312 (intramolecular), 2378, 5069, 5748 (intramolecular) (1995)

JACS 96 1133 (1974); 101 4743 (1979); 109 4335 (1987); 110 2655 (1988) (ArCl); 112 4324 (1990); 114 9694 (1992) (intramolecular); 115 3511, 5843, 6094 (intramolecular) (1993); 117 4722, 7834, 11590 (1995) (all intramolecular)

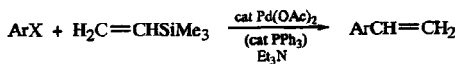
Syn 365 (1981)

CC 541 (1981); 1287 (1984); 1755 (1987)

JOMC 258 101 (1983)

TL 26 2667 (1985); 28 3039 (1987); 29 3903 (intramolecular), 4687 (intramolecular, benzofurans) (1988); 31 5781 (1990); 32 1753, 2121 (1991); 33 165 (1992); 34 1643, 3547, 3603, 8015 (1993); 35 939 (intramolecular), 3051, 3749 (intramolecular), 4103, 4133, 8919 (on polymer), 9537 (intramolecular) (1994); 36 1705, 4567, 4571, 5547, 6287, 6555 (intramolecular), 7047 (intramolecular), 7225, 8047 (iodonium salts), 8587 (intramolecular) (1995)

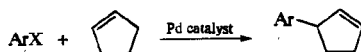
SL 405 (1990); 873 (1991); 715, 871 (1992); 743 (1993) (intramolecular); 189 (high pressure), 235, 759 (intramolecular), 839 (1994); 157 (1995)



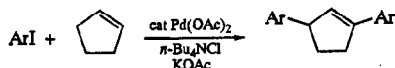
X = I, OTf

CL 1993 (1982)

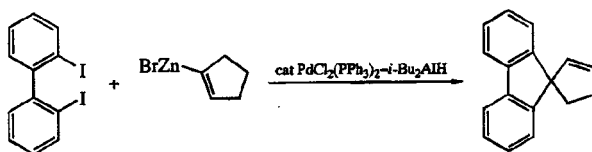
JOC 54 1773 (1989)



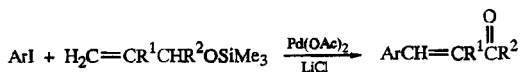
See page 236, Section 8.



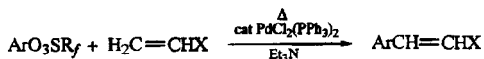
TL 30 2877 (1989)



TL 34 3551 (1993)

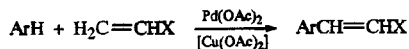


CL 403 (1981)



X = CN, CO₂Et

TL 27 1171 (1986); 32 2367 (1991)



X = R, Ar, CN, CO₂R, CONR₂

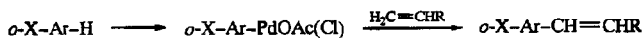
Tetr 25 4809, 4815, 4819 (1969)

Syn 524 (1973) (review)

CL 1230 (1979); 239 (1986) (ArH = uracil)

CC 859 (1981) (olefin = quinone)

JOC 46 851 (1981) (furan, thiophene, benzofuran, benzothiophene, indole; X = Ph, CO₂R, CN) 60 1486 (1995) (indole, X = CO₂R)



X

NHCOR

JOC 46 4416 (1981)

CH₂NR'₂

Acct Chem Res 2 144 (1969)

JOMC 102 239 (1975); 179 301 (1979); 182 537 (1979)

TL 355 (1977); 21 2757 (1980); 27 2169 (1986)

BCSJ 51 663 (1978); 52 142, 957 (1979)

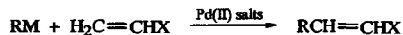
Tetr 37 173 (1981)

CH=N-*t*-Bu

TL 23 1957 (1982)

CH₂CH₂NMe₂

TL 27 1971 (1986); 33 4195 (1992)

RMX

ArMgX

Ar

CC 918 (1978)

ArTi(O₂CCF₃)₂

—

See page 365, Section 6.

K₂(PhSiF₅)CHO, CO₂R

Organomet 1 542 (1982)

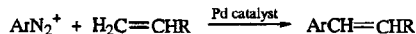
Ph₂CuM (M = Li, MgX)Ph, CO₂R

TL 4657 (1979)

R₂HgX (R = Me, CO₂R', Ar)

—

See page 400, Section 25.



CL 159 (1977)

Tetr 37 31 (1981)

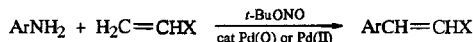
JOMC 270 277 (1984)

Syn 967 (1991)

JCS Perkin I 1943 (1993)

TL 36 4475 (1995)

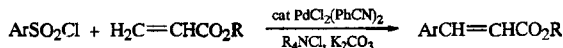
SL 441 (1995)

X = H, R, Ar, CO₂R

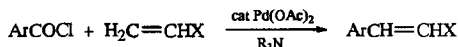
CL 551 (1980)

JOC 45 2359 (1980); 46 4885 (1981)

TL 35 8773 (1994)



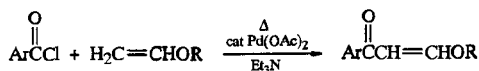
TL 30 975 (1989)

X = Ar, COR, CO₂R, CONR₂, CN, OR

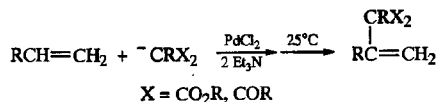
JOMC 233 267 (1982); 240 209 (1982)

JOC 53 235 (1988)

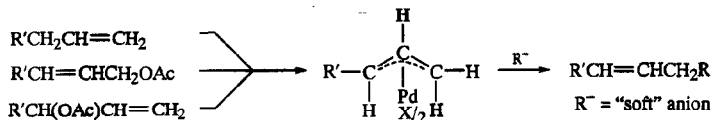
TL 32 1753 (1991)



TL 28 4215 (1987)



IACS 99 7093 (1977)



Reviews:

Tetr 33 2615 (1977); 42 4361 (1986); 51 975 (1995)

Acct Chem Res 13 385 (1980)

J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer Verlag, New York (1980)

"Comprehensive Organometallic Chemistry," Pergamon (1982), Vol 8, Chpt 57

Angew Int 24 283 (1985)

R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985)

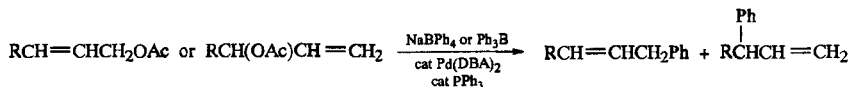
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Part 3.3, p 585

Tetr Asym 3 1089 (1992)

Some pertinent references:

JACS 100 3435 (1978); 101 1595 (1979) (intramolecular); 102 4743 (1980) (intramolecular); 104 6112 (1982) (intramolecular); 105 568 (1983) (intramolecular); 111 8281 (1989) (intramolecular); 112 4587 (1990) (stereochemistry); 113 670 (1991) (intramolecular); 114 4051 (1992); 115 6609 (1993)

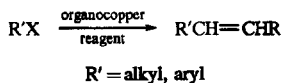
TL 2275 (1978) (intramolecular); 29 581 (1988); 33 717 (1992) (intramolecular)



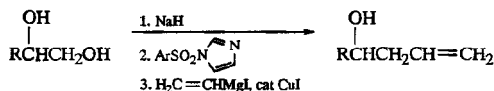
TL 31 7453 (1990)

22. Copper Reagents

See also page 362, Section 3; page 380, Section 17; page 386, Section 21; and page 599, Section 11.

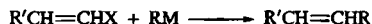


$\text{RCH}=\text{CHLi}$, CuI	Organomet 1 667 (1982) CC 925 (1986)
$\text{RCH}=\text{CHMgX}$, cat CuI	TL 1073 (1979) BCSJ 54 2831 (1981) JOC 51 4726 (1986)
$\text{RCH}=\text{CHMgX}$, cat Li_2CuCl_4	JACS 114 3910 (1992)
$\text{RCH}=\text{CHMnCl}$, cat Li_2CuCl_4	SL 45 (1993)
$\text{R}_7\text{CF}=\text{CFCu}$	JACS 108 4229 (1986)
$(\text{H}_2\text{C}=\text{CH})_2\text{CuLi}$	J Ind Chem Soc 45 1026 (1968) Helv 54 1939 (1971) JACS 93 7016 (1971)
$\text{RCH}=\text{CRCu}(\text{CN})\text{Li}$	JOC 58 4122 (1993)
$\text{RCH}=\text{CHCu}(\text{CN})\text{ZnX}$	JACS 114 3983 (1992)
$\text{ThCu}(\text{CR}=\text{CH}_2)(\text{CN})\text{Li}$	JOC 59 6322 (1994)
$(\text{H}_2\text{C}=\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2$	JACS 109 1186 (1987)
$[\text{RCH}=\text{CHCuC}\equiv\text{CC}(\text{CH}_3)_3]\text{Li}$	TL 23 739 (1982)



JOC 60 8122 (1995)

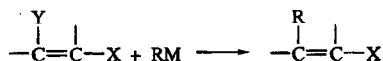
For other organometallics, see page 88, Section 2.1 and page 585, Section 1.




Review: Org Rxs 41 135 (1992)

<u>X</u>	<u>RM</u>	
halogen	RLi or RMgX , cat CuBr	Compt Rend C 278 967 (1974)
	RMgX , cat Li_2CuCl_4	JOMC 128 1 (1977) JACS 109 1856 (1987)
	RCu ($\text{R} = \text{Ph}$, $\text{CH}_2\text{C}\equiv\text{CSiMe}_3$, CH_2CMe_3)	JOMC 93 415 (1975)
	$\text{C}_6\text{F}_5\text{CF}_2\text{CF}_2\text{Cu}$	JACS 114 4402 (1992)
	$\text{RC}\equiv\text{CCu}$	See page 599, Section 11.
	R_2CuLi	JACS 89 3911 (1967); 90 5615 (1968); 94 2520 (1972) JOC 35 1715 (1970) Org Rxs 19 1 (1972) (review)
	$\text{RCu}(\text{CN})\text{ZnX}$	TL 33 4495 (1992)
	$\text{ArCu}(\text{CN})\text{ZnX}$	SL 849 (1994) TL 35 1047 (1994)

<u>X</u>	<u>RM</u>	
OTf	R ₂ CuM (M = Li, MgX; R = 1° alkyl, aryl)	TL 21 4313 (1980); 32 157 (1991) JACS 110 5768 (1988); 115 1676, 8873 (1993) JOC 54 3374 (1989); 55 5854 (1990); 60 191, 2656 (1995) SL 151 (1995)
	1.5 RLi, CuCN R ₂ Cu(CN)Li ₂ ThCuR(CN)Li ₂	TL 29 1197 (1988) Heterocycles 26 355 (1987) JACS 117 10239 (1995)
OPO(OPh) ₂	R ₂ CuLi	TL 4405 (1976)
SPh	<i>t</i> -Bu ₂ CuLi	JOC 54 1836 (1989)
SO ₂ Ph	<i>t</i> -Bu ₂ CuLi	JOC 54 1836 (1989)



<u>X</u>	<u>Y</u>	<u>RM</u>	
SiMe ₃	OPO(OPh) ₂	R ₂ CuLi R ₂ Cu(CN)Li ₂	JOC 54 743 (1989) JOC 54 743 (1989)
COR	halogen	RMgX, CuX R ₂ CuLi R ₂ CuMgX R ₂ CuZnX (Me ₃ SiCH ₂) ₂ CuLi RCu(SPh)Li	JCS Perkin I 593, 599 (1981) CC 671 (1986) JOC 41 636, 3629 (1976); 46 2089 (1981) Can J Chem 60 1256 (1982) SL 186 (1993) SL 186 (1993) TL 30 3327 (1989) JOC 40 2694 (1975) TL 3233, 3237 (1976) CC 1033 (1978) (R = Me ₃ Sn) JCS Perkin I 593 (1981) Can J Chem 60 1256, 2965 (1982) TL 33 6751 (1992) TL 33 6751 (1992) TL 29 6693 (1988); 30 5069 (1989); 31 1833, 7575 (1990); 33 7515 (1992) JOC 54 5202 (1989); 55 4791 (1990); 58 588 (1993) JOC 53 5789 (1988) TL 31 4413 (1990) JACS 114 3983 (1992) JOC 57 1956 (1992); 60 3311 (1995) TL 34 5261 (1993) SL 410 (1994)
		RCu(CN)Li R ₂ Cu(CN)Li ₂ RCu(CN)ZnX	
		ArCH ₂ Cu(CN)ZnX ArCu(CN)ZnX	
		R ₂ Zn, CuCN·2LiCl	

OAc	ArCH ₂ Cu·ZnI ₂	JOC 58 2694 (1993)
	R ₂ CuLi	TL 2071 (1973)
		JOC 41 3629 (1976)
	R ₂ CuLi·BF ₃	JOC 58 3953 (1993)
	R ₂ CuLi	Ind J Chem 12 325 (1974)
	R ₂ CuLi	Can J Chem 57 1431 (1979)
	R ₂ CuLi	Ind J Chem 12 325 (1974)
	 NCuR(CN)Li ₂	TL 33 1041 (1992)
	SR	TL 36 1925 (1995)
	ArCH ₂ MgX, CuCl, (Me ₃ SiCl) RMgX, CuBr RMgX, CuCN	Syn 320 (1976) Syn Commun 6 209 (1976) JOC 51 4807 (1986) CC 907 (1973) TL 3817 (1973) Acta Chem Scand B 33 460 (1979) CL 815 (1982) JOC 48 2786 (1983); 51 4687 (1986); 52 110 (1987) JACS 107 4679 (1985) TL 32 7567 (1991) TL 23 3751 (1982) JACS 107 4679 (1985) JOC 48 2786 (1983) JACS 107 4679 (1985) JOC 51 4687 (1986) JOC 51 4687 (1986) SL 180 (1995) SL 180 (1995)
	R ₂ CuLi	
TeR	R ₂ CuMgX	
	RCu(SPh)Li	
	(RCuC≡CCMe ₂ OMe)Li	
	R ₂ Cu(SCN)Li ₂	
	R ₂ Cu(CN)Li ₂	
	R ₂ CuZnCl (R = 1° alkyl, aryl)	
	R ₂ Cu(CN)(ZnCl) ₂	
	(R = 1° alkyl, aryl)	
CO ₂ R	F	RMgX, CuBr
	Cl	R ₂ CuLi
		TL 35 9259 (1994) JOC 43 3974 (1978); 46 2089 (1981) TL 3369 (1977) TL 34 3139 (1993) TL 3465 (1975) TL 2071 (1973); 27 959 (1986) Syn Commun 3 321 (1973) JOC 43 3974 (1978) Ann 1173 (1982) TL 925 (1974) JOC 43 3974 (1978) TL 25 1333, 1643 (1984); 28 731 (1987) Can J Chem 57 1431 (1979); 59 2239 (1981) Ann 1173 (1982)
	Br	(R ₃ BMe)Li, CuI
	I	CF ₃ Cu
	O ₂ CR	RLi, CuI·n-Bu ₃ P R ₂ CuLi
OCO ₂ R		R ₂ CuLi·n-Bu ₃ P
		R ₂ CuLi
	OPO(OEt) ₂	MeMgCl, MeCu
OPO(OEt) ₂		R ₂ CuLi

XYRM

CC 421 (1982); 24 (1987)
 JOC 49 1707 (1984); 52 1106
 (1987); 55 5631 (1990); 56
 3973 (1991); 60 7879 (1995)
 JACS 107 2712 (1985)
 TL 27 5555 (1986); 31 2239
 (1990)
 Org Syn Coll Vol 7 351 (1990)
 TL 34 7229 (1993)
 JOC 51 3247 (1986)
 TL 31 3291, 3389 (1990)
 JOC 58 2296 (1993)
 JOC 58 2296 (1993)
 TL 31 3291, 3389 (1990)
 CL 1097 (1973); 705, 1425
 (1974)
 Syn 320 (1976)
 CC 907 (1973)
 JOC 50 2730 (1985); 57 2018
 (1992)
 JACS 107 4679 (1985)
 JOC 55 5446 (1990)
 JOC 55 5446 (1990)
 TL 32 441 (1991)

OSO₂F
 OTf

R₂CuMgBr
 R₂CuLi
 R₂CuLi, BF₃·OEt₂
 R₂CuMgX
 R₂Cu(CN)Li₂
 RMgX, CuX

SR

R₂CuLi

RCu(SPh)Li

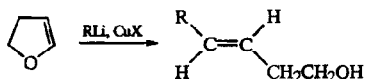
(CO₂R)₂SO₂Ph

RCu(CN)Li
 RCu(CN)ZnI

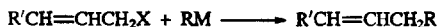
NO₂SO₂Ph

RCu(CN)ZnI

For related reactions, see page 382, Section 20, and page 386, Section 21.



See page 1061, Section 4.3.



Review: Org Rxns 41 135 (1992) (organocopper reagents)

For allylic rearrangements, see page 236, Section 8.

XRM

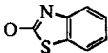
Cl

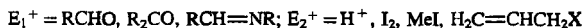
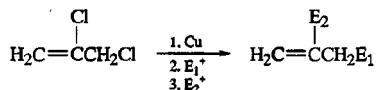
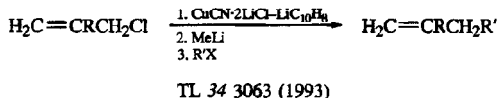
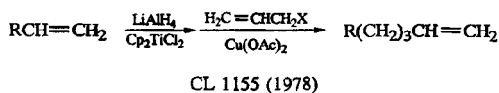
RMgBr, cat CuCl·2LiCl
 RMgBr, cat CuX (X = Cl, I)
 RMgBr, cat Cu(acac)₂
 RMgX (X = Cl, Br), cat
 Li₂CuCl₄

RCu

JOC 59 4126 (1994)
 Helv 65 684 (1982)
 Tetr 39 3283 (1983)
 TL 23 3115 (1982)
 Helv 65 684 (1982)
 CC 590 (1986)
 SL 219 (1993)

	R_2CuLi ($R = 1^\circ$ alkyl)	TL 4439 (1976) JACS 112 6615 (1990) JOC 59 2025 (1994)
	$R_2CuLi \cdot SMe_2$ ($R = 1^\circ$ alkyl, vinyl)	TL 2705 (1978)
	R_2CuMgX	JOC 57 5250 (1992)
	$RCu(CN)ZnX$	TL 31 1829, 7575 (1990)
Cl, Br	$C_6F_5CF_2CF_2Cu$	JACS 114 4402 (1992)
	$NCCH_2CH_2Cu(CN)ZnI$	TL 29 2395 (1988); 30 5069 (1989)
Br	$RMgBr$, cat CuX ($X = Br, I$)	CL 177 (1982) BCSJ 56 1446 (1983)
	$ArMgBr$, CuI	JOC 50 2427 (1985)
	RCu ($R = sec\text{-}Bu, t\text{-}Bu$)	JOC 49 1840 (1984)
	Ar_2CuLi	JCS Perkin I 2909 (1982) JOC 49 1840 (1984); 52 3394 (1987)
	$[ArCuC \equiv CMe_2OMe]Li$	TL 27 1607 (1986)
	$ArCu(CN)ZnX$	JACS 114 3983 (1992)
	$R_2Zn, CuCN \cdot 2LiCl$	SL 410 (1994)
I	Ar_2CuLi	JOC 57 5247 (1992)
OTs	$RMgBr$, cat Li_2CuCl_4	Helv 65 684 (1982)
OAc	$RMgBr$, cat $CuBr$	Syn 804 (1983)
	$RMgBr$, cat CuI	Helv 65 684 (1982)
	$RMgBr$, cat $CuCN$	JACS 112 6615 (1990)
	$RMgBr$, cat $Cu(acac)_2$	Tetr 39 3283 (1983)
	$RMgX$, cat Li_2CuCl_4	Angew Int 13 82 (1979)
	($R = 1^\circ$ alkyl, aryl)	Helv 65 684 (1982) TL 24 5103 (1983); 28 1175 (1987); 31 5771 (1990); 35 5931 (1994) Syn 804 (1983) CC 827 (1987) JACS 112 6615 (1990)
	$RMgX$, cat $CuSAr$	TL 35 5931 (1994)
	$RCu \cdot (AlCl_3)_n$ ($R = n\text{-}Bu$)	Syn Commun 10 119 (1980) ($R' = CO_2R$)
	R_2CuLi ($R = Me, n\text{-}Bu$)	JOMC 136 103 (1977) JOC 46 5304 (1981); 48 721, 3986 (1983) TL 23 3093 (1981)
	R_2CuLi ($R = Ph$)	JACS 101 4413 (1979)
	$Li_2Cu_3Me_5$	TL 23 3093 (1982)
O_2CCMe_3	$RMgX$, cat $CuCl$	JOC 54 2369 (1989)
	$PhMgX$, cat $CuCN$	JOC 54 2369 (1989)
	R_2CuLi	Can J Chem 61 632 (1983) JOC 52 897 (1987); 54 2369 (1989)

<u>X</u>	<u>RM</u>	
OCO ₂ Et	RMgBr, cat CuBr	Syn 804 (1983)
OCNMe ₂	RMgX, cat CuI	JOC 51 5456 (1986)
OPO(OEt) ₂	RMgBr, cat CuX (X = Br, I)	CL 177 (1982)
	RMgX, CuI	BCSJ 56 1446 (1983)
	1° RMgX, CuBr	JACS 106 723, 6006 (1984)
		JOMC 231 179 (1982)
SO ₂ Ph		JCS Perkin I 2953 (1983)
	RMgX (R = 1° alkyl), cat Cu(acac) ₂	TL 2393 (1979)
	R ₂ CuLi	Tetr 39 3283, 3289 (1983)
		Tetr 39 3283 (1983)
		JACS 112 6615 (1990)
SO(NMe)Ph	RCu·BF ₃	JACS 113 1442 (1991)
	RCu, BF ₃ ·SMe ₂ , LiI	JACS 117 2453 (1995)
	RCu, LiI	JACS 117 2453 (1995)
	R ₂ CuLi	JACS 113 1442 (1991)
	R ₂ CuLi, LiI	JACS 117 2453 (1995)
⁺ SMe ₂ Br ⁻	RMgBr, cat CuBr	Syn 804 (1983)
⁺ NR' ₃ X ⁻	RMgBr, cat CuBr	Syn 804 (1983)
	RMgX, cat Li ₂ CuCl ₄	JOC 52 2947 (1987)
		TL 31 1865 (1990)
	R ₂ CuLi	TL 21 67 (1980)
		JOC 52 3683 (1987)



TL 33 6575 (1992)



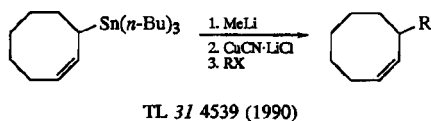
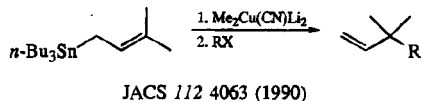
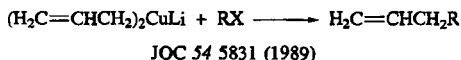
Reagent

cat Li₂CuCl₄

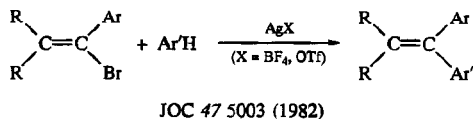
Syn Commun 24 1557 (1994)

TL 36 8565 (1995)

cat Li_2CuCl_3	TL 36 8565 (1995)
cat CuI	TL 1181 (1977)
	Syn Commun 11 859 (1981)
	JOC 59 943 (1994)
CuBr·SMe ₂	SL 573 (1991)

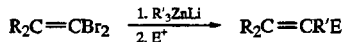
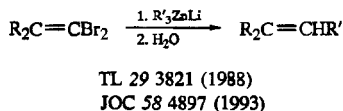


23. Silver Reagents

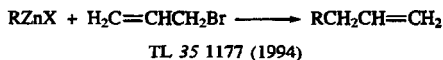


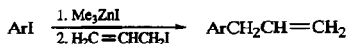
24. Zinc Reagents

For transition metal-catalyzed cross-coupling of organozinc compounds, see the appropriate transition metal (Ni: page 382, Section 20; Pd: page 386, Section 21; Cu: page 392, Section 22).

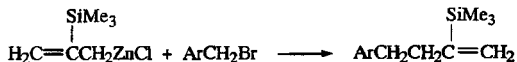


E^+ = Pd catalyst plus ArBr, vinylic Br, RCOCl or ClCO_2R
JOC 58 4897 (1993)

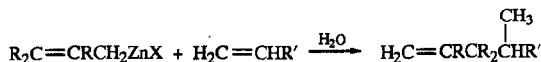




JOC 59 4717 (1994)

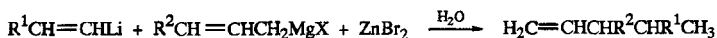


SL 277 (1993)



JOMC 221 123, 131 (1981)

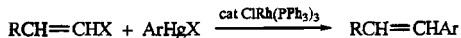
JOC 59 4154 (1994)



SL 633 (1992)

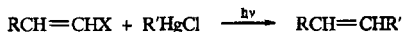
25. Mercury Reagents

See also page 386, Section 21.



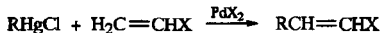
X = halogen

JOC 48 4377 (1983)

X = Cl, Br, I, PhS, *n*-Bu₃Sn

JACS 106 4622 (1984); 110 3530 (1988)

TL 26 4975 (1985); 28 6113 (1987)

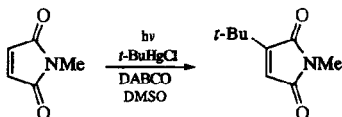
R = Me, CO₂R', Ar; X = CHO, COR, CO₂R, CN, Ar

R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer Verlag, New York (1985), Chpt 7 (review)

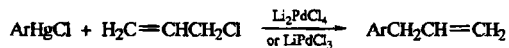
JACS 111 6966 (1989); 113 359 (1991)

JOC 54 4801 (1989)

SL 873 (1991)



SL 87 (1990)

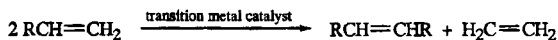


JACS 90 5531 (1968)

JOC 54 4141 (1989)

SL 27 (1995)

6. Olefin Metathesis



Reviews:

Comprehensive Organometallic Chemistry 8 499 (1982)

K. J. Ivin, "Olefin Metathesis," Academic Press, London (1983)

Chemtech 758 (1983)

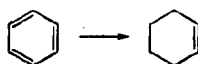
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 5, Part 9.3, p 1115

For intramolecular reactions, see page 559, Section 8.

6. ARENE, ALKYNE AND DIENE ADDITION REACTIONS

See also page 463, Section 7 for the synthesis of dienes and polyenes.

1. Hydrogen Addition

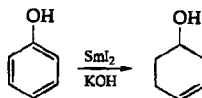


$[\text{Os}(\text{NH}_3)_5]^{2+} / \text{H}_2$, cat Pd-C/[O]

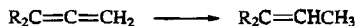
JACS 110 7906 (1988); 112 2682 (1990)

Li, RNH₂

JACS 77 3230 (1955)



TL 35 4169 (1994)



H₂, cat Pd-CaCO₃, Pb(OAc)₂, quinoline

JACS 106 1138 (1984)

Na-K, crown ether, toluene

JACS 115 497 (1993)



Review: Chem Rev 31 77 (1942)

H₂, cat Et₄N[HCr₂(CO)₁₀]

TL 32 1199 (1991)

H₂, cat RuCl₂(PPh₃)₃

BCSJ 41 254 (1968)
CL 1083 (1977)

H₂, cat K₃[Co(CN)₅H]

TL 115 (1979)
JOC 45 3860 (1980)

H₂, cat CoCl₂·6H₂O-MCl₃·7H₂O (M = La, Ce, Yb)-β-cyclodextrin-KCN-KCl-OH⁻

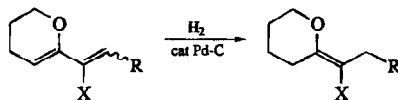
JOC 55 1854 (1990)

H ₂ , cat ClRh(PPh ₃) ₃	Discuss Faraday Soc 46 60 (1968)
H ₂ , cat [Ir(COD)(py)(PCy ₃)]PF ₆	JOC 54 3207 (1989)
H ₂ , cat Ni(acac) ₂ -Al ₂ Et ₃ Cl ₃ -PPh ₃	BCSJ 55 343 (1982)
H ₂ , cat Pd(O)-polymer	Israel J Chem 17 269 (1978)
H ₂ , cat polymer-Pd(OAc) ₂	JOMC 335 125 (1987)
H ₂ , cat PdCl ₂ ·Ph ₂ P-montmorillonite	JOC 54 2997 (1989)
H ₂ , cat [<i>t</i> -Bu ₂ PPd(<i>t</i> -Bu ₂ PH)] ₂ -O ₂	TL 36 5673 (1995)
H ₂ , cat Cp* ₂ YMe(THF)	JOC 57 3266 (1992)
Li, NH ₃	JOC 39 2931 (1974); 55 4403 (1990)
Li, NH ₃ , <i>t</i> -BuOH	JOC 41 3524 (1976) TL 35 6101 (1994)
Na, NH ₃	JACS 84 4347 (1962)
Na, NH ₃ , <i>t</i> -BuOH	JOC 41 3524 (1976) JACS 110 4062 (1988)
K, NH ₃ , <i>t</i> -BuOH	JOC 41 3524 (1976)
<i>i</i> -Bu ₂ AlH	TL 36 8359 (1995)
R ₃ SnH, cat [(<i>p</i> -BrC ₆ H ₄) ₃ N]SbCl ₆	JACS 114 5457 (1992)



Review: Syn 643 (1993) [ArH-Cr(CO)₃]

<u>X</u>	<u>Reagent(s)</u>	
H or R	H ₂ , cat C ₆ H ₅ CO ₂ CH ₃ ·Cr(CO) ₃	JACS 90 2446 (1968) TL 1919 (1968); 26 3491 (1985) JOC 34 3930, 3936 (1969); 49 4096 (1984)
	H ₂ , cat naphthalene·Cr(CO) ₃	TL 28 1893 (1987); 29 1417 (1988) JOC 53 1227 (1988)
R	(Me ₂ SiH) ₂ O, HOAc, cat Pd ₂ (DBA) ₃ ·CHCl ₃ , cat (<i>o</i> -Tol) ₃ P	TL 30 4657 (1989)
COR	H ₂ , cat C ₆ H ₅ CO ₂ CH ₃ ·Cr(CO) ₃	JACS 106 3875 (1984) (cis product)
COR, CO ₂ R	<i>i</i> -Bu ₂ AlH, cat MeCu, HMPA / H ₂ O	JOC 51 537 (1986)
CO ₂ R	H ₂ , cat C ₆ H ₅ CO ₂ CH ₃ ·Cr(CO) ₃	TL 1919 (1968); 28 5841 (1987) JACS 90 2446 (1968)
	Et ₃ SiH, cat ClRh(PPh ₃) ₃	Syn Commun 15 965 (1985)
	Na ₂ S ₂ O ₄	CL 715 (1982) (trans product)
OAc	H ₂ , cat naphthalene·Cr(CO) ₃	TL 26 6497 (1985)



X = CO₂Me, CN; stereoselective

JACS 111 643 (1989)



Zn, BrCH₂CH₂Br

Syn Commun 20 3421 (1990)

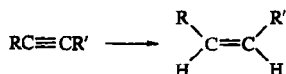
Zn, BrCH₂CH₂Br, CuBr, LiBr

Syn Commun 20 3421 (1990)

TL 35 5559 (1994)

Zn(Cu), H₂O, Et₂O

Syn 400 (1981)



Reviews:

Chem Rev 31 77 (1942)

Syn 457 (1973) (hydrogenation)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Parts 3.1-3.3, pp 417-470

Li/H₂O

JACS 92 2268 (1970) (R, R' = Ph)

JOC 35 1702 (1970) (R, R' = Ph)

Angew Int 25 167 (1986) [R, R' = (CH₂)₆]

Zn, H₂O, MeOH, THF (enyne)

JACS 116 5050 (1994)

Zn (ZnBr₂-K), H₂O, MeOH, THF (enyne, diyne, propargylic alcohol)

Helv 62 135 (1979)

TL 32 299 (1991)

JACS 114 4658 (1992)

Zn, BrCH₂CH₂Br, EtOH (ArC≡CH, enyne, diyne)

CC 735 (1984)

Syn Commun 20 3421 (1990)

TL 33 4229 (1992)

Zn, BrCH₂CH₂Br, CuBr, LiBr, EtOH (propargylic and homopropargylic alcohol and amine, propargylic ether, enyne, diyne)

CC 735 (1984)

Syn Commun 20 3421 (1990)

TL 33 4229 (1992)

Zn, Cu(OAc)₂, AgNO₃, MeOH (enyne)

Helv 70 1025 (1987)

TL 30 4951 (1989); 32 2651 (1991); 33 2681 (1992);

35 3543 (1994); 36 4245 (1995)

SL 217 (1993)

Zn(Cu), MeOH (aryl alkyne or propargylic alcohol)

TL 21 1069 (1980)

Zn, KCN, H₂O, ROH (enyne)

Helv 58 1016 (1975); 60 48 (1977)

JACS 109 8051 (1987)

TL 31 2295 (1990)

- Zn, HOAc, MeOH TL 28 5395 (1987)
- Zn, NbCl₅/NaOH, H₂O TL 31 365 (1990)
JOC 57 1615 (1992)
- Zn, TaCl₅/NaOH, H₂O TL 31 365 (1990)
JOC 57 1615 (1992)
- SmI₂, cat CoCl₂·4PPh₃, ROH TL 32 5559 (1991)
- H₂, cat ClRh(PPh₃)₃ TL 34 3663 (1993)
- H₂, cat [Rh(NBD)(PR₃)₃]PF₆ JACS 98 2143 (1976)
- H₂, cat nickel boride P-2 JACS 85 1005 (1963)
CC 553 (1973)
JOC 38 2226 (1973); 46 1263 (1981)
TL 33 5757 (1992)
- H₂, cat Ni(OAc)₂-NaBH₄, cat EDA JOC 57 1952 (1992)
- H₂, cat Ni graphite, EDA JOC 46 5340, 5344 (1981)
- H₂, cat Ni₄[CNC(CH₃)₃]₇ Pure Appl Chem 50 941 (1978)
- H₂, cat NaH-Ni(OAc)₂-t-AmOH TL 3965 (1977)
JOC 45 1937, 1946 (1980)
- H₂, cat Pd polymer J Catalysis 57 315 (1979)
- H₂, cat Pd graphite, EDA CC 540 (1981)
- H₂, cat Pd on tungsten film JOC 52 3132 (1987)
- H₂, cat Pd-C JOC 59 2282 (1994)
- H₂, cat Pd-CaCO₃, py JACS 111 636 (1989)
- H₂, cat Pd-CaCO₃, quinoline JOC 48 2270 (1983)
- H₂, cat Pd-CaCO₃, Pb(OAc)₂, quinoline (Lindlar) Helv 35 446 (1952)
JACS 78 2518 (1956); 107 1028 (1985);
113 2071 (1991)
Org Syn Coll Vol 5 880 (1973)
JOC 41 3497 (1976); 43 3435 (1978); 52 3126
(1987); 57 1242 (1992)
SL 558 (1992)
- H₂, cat Pd-CaCO₃, cat MnCl₂, Pb(OAc)₂, quinoline Tetr 39 2315 (1983)
- H₂, cat Pd-BaSO₄, py JOC 50 2309 (1985)
- H₂, cat Pd-BaSO₄, quinoline JACS 78 2518 (1956); 110 4718 (1988); 111
636 (1989)
Org Syn 64 108 (1985)
JOC 51 4158 (1986); 57 1047 (1992)
Org Syn Coll Vol 7 226 (1990)
- H₂, cat PdCl₂, DMF Ber 109 531 (1976)
- H₂, cat PdCl₂·Ph₂P-montmorillonite JOC 54 2997 (1989)

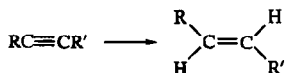
H ₂ , cat NaH-Pd(OAc) ₂ - <i>t</i> -AmOH, quinoline	JOC 49 4058 (1984)
(Et ₃ NH)O ₂ CH, cat Pd-C (R = aryl, vinyl)	JOC 45 4926 (1980)
LiH, ZnI ₂ , cat Cp ₂ TiCl ₂ /H ₂ O	JOC 60 290 (1995)
MgH ₂ , CuI or CuO- <i>i</i> -Bu	JOC 43 757 (1978)
2 <i>n</i> -BuMgX, CuI/H ₂ O	JOC 41 4089 (1976)
<i>i</i> -BuMgX (X = Cl, Br), Cp ₂ TiCl ₂ /H ₃ O ⁺	TL 22 85 (1981) CC 1126 (1982) JACS 109 1469 (1987)
BH ₃ or R ₂ BH/HOAc	JACS 81 1512 (1959); 83 3834 (1961); 93 3395 (1971); 109 2138 (1987); 110 649, 1529, 8223 (1988) Tetr 37 2617 (1981) JOC 51 4512, 4514 (1986); 58 4823 (1993) TL 30 6487 (1989) (1,3-diyne); 31 5113 (1990); 35 9497 (1994)
CIBH ₂ /HOAc	JOC 38 1617 (1973)
CB/HOAc	JACS 94 4370 (1972)
CB/H ₂ O/HOCH ₂ CH ₂ OH/HOAc	JACS 107 3626 (1985)
9-BBN/MeOH	JOC 51 4512 (1986)
R ₂ BH/ <i>n</i> -BuLi/NaOH	JOC 41 3484 (1976)
R ₂ BH/cat Pd(OAc) ₂	CC 702 (1978) BCSJ 53 1670 (1980)
NaBH ₄ , cat PdCl ₂	CC 515 (1983)
<i>i</i> -Bu ₂ AlH/H ₂ O	Ann 629 222 (1960) JOC 43 2739 (1978)
LiAlH ₄ , TiCl ₄	TL 15 (1976)
LiAlH ₄ , NiCl ₂	TL 4481 (1977)
NaAlH ₄ , NbCl ₅	CL 157 (1982)
Cl ₃ SiH/KF/CuF ₂ ·2H ₂ O	TL 1141 (1979)
(Me ₂ SiH) ₂ O, HOAc, cat Pd ₂ (DBA) ₃ ·CHCl ₃ , cat (<i>o</i> -Tol) ₃ P	TL 30 4657 (1989)
(EtO) ₃ SiH, cat RhCl ₃ ·3H ₂ O, cat Cu(NO ₃) ₂ ·2.5H ₂ O, H ₂ O, THF	JOC 57 4786 (1992)
(EtO) ₃ SiH, cat Pd(OAc) ₂ , H ₂ O, THF	TL 31 4719 (1990) JOC 55 3452 (1990)
hydrosilane-SiO ₂ , cat Pd(PPh ₃) ₄ , HOAc	TL 35 1507 (1994)
Ph ₃ SnH/ <i>n</i> -BuLi/H ₂ O	JACS 112 3156 (1990)
Cp ₂ ZrHCl/H ₂ O	TL 31 7257 (1990); 33 5861 (1992) (R = SnR ₃)

LaNi₅H₆

JOC 52 5695 (1987)

[(PPh₃)CuH]₆, H₂O

TL 31 2397 (1990)



Reviews:

Chem Rev 31 77 (1942)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, parts 3.1-3.3, pp 417-470

Li/H₂O

Angew Int 25 167 (1986)

Li, CH₃NH₂

CC 634 (1968)

Na, NH₃

JACS 63 216, 2683 (1941); 65 2020 (1943); 74 3643 (1952)

JCS 3558 (1955)

Syn 567 (1972); 616 (1973); 114 (1979)

Na, NH₃, *t*-BuOH

JOC 58 5063 (1993)

Yb, NH₃

JOC 43 4555 (1978)

i-Bu₂AlH/H₂O

TL 3145 (1979) (3° propargylic amines)

LiHAlMe(*i*-Bu)₂/H₂O

JACS 89 5085 (1967)

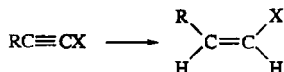
CrSO₄, H₂O

JACS 86 4358 (1964)

JOC 51 253 (1986)



CL 363 (1984)

XReagent(s)

Br

Cy₂BH/HOAc

JACS 89 5086 (1967)

I

Cy₂BH/HOAc

JACS 89 5086 (1967); 107 713 (1985)

(Sia)₂BH/HOAc

JACS 110 5383 (1988)

KO₂CN=NCO₂K, HOAc

JACS 94 9256 (1972); 100 6211 (1978)

JOC 40 1083 (1975); 57 6090 (1992); 59 5662 (1994)

TsNHNH₂, NaOAc, H₂O, THF

Angew Int 28 587 (1989)

Cl, Br, I

Cy₂BH or 9-BBN/HOAc

JOC 54 6064 (1989)

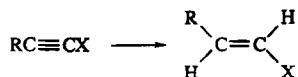
OR

NaH₂Al(OCH₂CH₂OCH₃)₂,
ROH

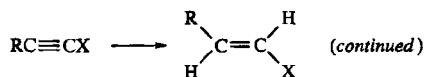
JACS 112 9388 (1990)

TL 33 2863 (1992)

CR ₂ OH	<i>i</i> -BuMgX, cat Cp ₂ TiCl ₂ /H ₂ O	CC 718 (1981)
CO ₂ R	NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂ , CuBr	JOC 40 3619 (1975)
SR	LiAlH(O- <i>i</i> -Bu) ₃ , CuBr	JOC 60 7690 (1995)



<u>X</u>	<u>Reagent(s)</u>	
Cl	LiAlH ₄	JACS 101 5101 (1979)
OR	LiAlH ₄	JOC 52 2919 (1987) JACS 112 9388 (1990) TL 33 2863 (1992)
	NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂	JACS 112 9388 (1990)
SR	LiAlH ₄	JACS 111 4514 (1989) JOC 60 7690 (1995)
CH ₂ NH ₂ , CH ₂ NHR	LiAlH ₄	JOC 52 5044 (1987)
CH ₂ NHBoc	NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂	SL 368 (1994)
CH ₂ OH	Na, NH ₃ LiAlH ₄	JOC 41 3497 (1976) JACS 71 4140 (1949); 89 4245 (1967); 92 4898 (1970); 103 4483 (1981); 106 7614 (1984); 107 1028 (1985); 111 1057 (1989); 114 6850 (1992) JCS 3185 (1950); 1094 (1952); 1584 (1953); 1854 (1954); 2754 (1957) JOC 31 528 (1966); 39 968 (1974); 47 4595 (1982); 51 4158 (1986); 52 3798 (1987) CC 1017 (1968) TL 27 5857 (1986); 36 8829 (1995) SL 453 (1990); 279 (1991)
	NaAlH ₂ (OCH ₂ CH ₂ OCH ₃) ₂	JOC 41 3497 (1976); 43 3435 (1978); 47 4595 (1982); 51 1155 (1986); 60 6046 (1995) Org Syn 64 182 (1985) JACS 109 1186, 1469, 2205 (1987); 113 5365 (1991) TL 28 527, 803, 2041 (1987); 29 143 (1988) Org Syn Coll Vol 7 524 (1990)
	NaAlH ₂ (OCH ₂ CH ₂ OEt) ₂ (?) CrSO ₄ , H ₂ O	JOC 51 863 (1986) JACS 86 4358 (1964)
(CH ₂) _n OH	LiAlH ₄	Syn 561 (1977) (<i>n</i> = 2, 6, 7) Ber 114 292 (1981) (<i>n</i> = 7) JOC 59 8307 (1994) (<i>n</i> = 2) TL 36 5471, 8829 (1995) (both <i>n</i> = 2)



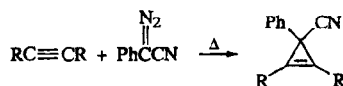
<u>X</u>	<u>Reagent(s)</u>	
CHO, COR, CO ₂ H, CO ₂ R	H ₂ O, cat Ph _n P- (<i>m</i> -C ₆ H ₄ SO ₃ Na) _{3-n} (<i>n</i> = 0, 2)	TL 34 4331 (1993)
COR	CrCl ₂ , H ₂ O, THF	Syn 184 (1986)
	CrSO ₄ , H ₂ O, DMF	Syn 184 (1986)
	[Cr(OAc) ₂ ·H ₂ O] ₂ , H ₂ O, THF	JACS 117 8106 (1995)
COR, CO ₂ Me	<i>i</i> -Bu ₂ AlH, HMPA, (cat MeCu)	JOC 52 1624 (1987)
CO ₂ H	<i>m</i> -NaO ₃ SC ₆ H ₄ PPh ₂ , H ₂ O/ Na ₂ CO ₃ or NaOH/HCl	TL 29 4577 (1988)
CO ₂ R	electrolysis, PhCO ₂ H	SL 408 (1990)
CN	LiAlH ₄	Syn 430 (1979)

2. Alkylation and Functionalization

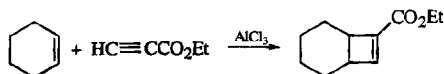
Review: P. Perlmutter, "Conjugate Addition Reactions in Organic Synthesis." Tetrahedron Organic Chemistry Series, Vol 9, Pergamon, New York (1992)

See also page 655, Section 4, for the synthesis of vinylic halides, and page 545, Section 9.

2.1. Thermal or Lewis Acid-Promoted



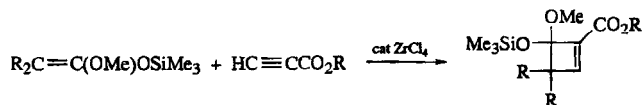
JACS 80 5991 (1958); 114 6603 (1992)



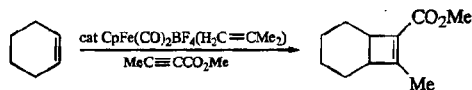
JOC 41 3061 (1976); 44 248, 253, 2802 (1979); 45 2773 (1980)

JACS 101 5283 (1979)

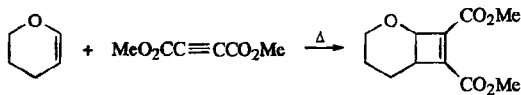
Acct Chem Res 13 426 (1980)



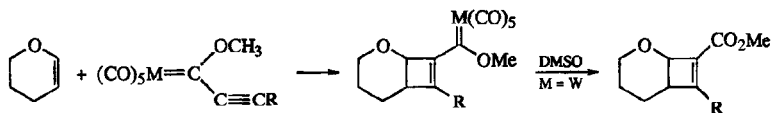
TL 29 6443 (1988)



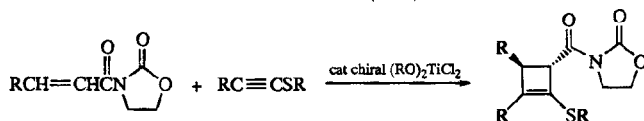
Organomet 1 397 (1982)



TL 28 1501 (1987)

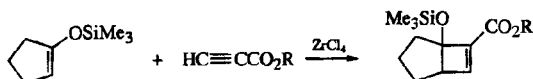
 $\text{M}=\text{Cr}, \text{W}$

JACS 110 8727 (1988)

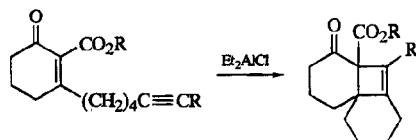


CL 1295 (1990)

JACS 114 8869 (1992)



TL 31 5027 (1990); 33 3879 (1992)

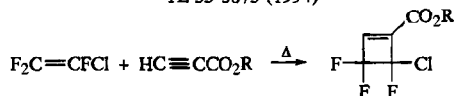


TL 36 5499 (1995)

 $\text{X}=\text{R}, \text{OR}$

SL 403 (1994)

TL 35 3073 (1994)



TL 32 7265 (1991)

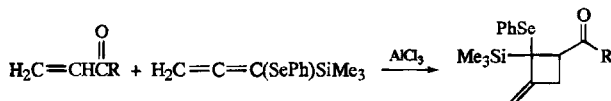


X = COR, CO₂R, CN

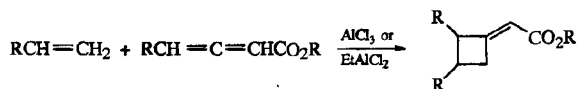
CL 2091 (1990)

JACS 114 8869 (1992)

TL 34 8123 (1993)



JOC 57 5610 (1992)



JOC 45 5017 (1980); 51 3643 (1986)

TL 22 1953 (1981)

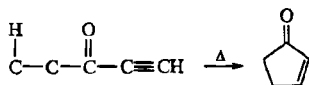


TL 2231 (1978)

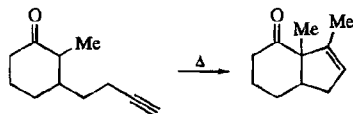
JACS 104 3670 (1982); 106 152 (1984); 107 3626 (1985); 115 3776 (1993) (intramolecular); 117 7071 (1995) (intramolecular)

JOC 48 1500 (1983); 49 2381 (1984); 55 711 (1990); 56 3781, 3795, 6216 (1991); 57 12 (1992)

Acct Chem Res 24 63 (1991)

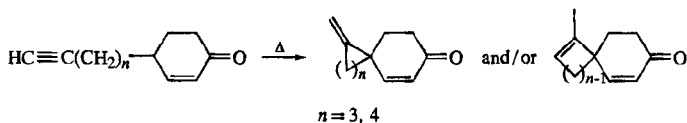


Helv 62 852 (1979); 65 13, 2413, 2517 (1982)



JACS 110 3315 (1988)

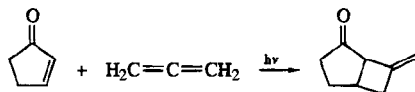
TL 29 2147 (1988)



TL 30 4329 (1989)

2.2. Photochemical

See also the following section.



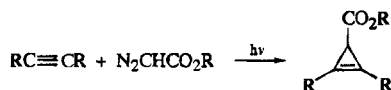
TL 3695 (1964)

Tetr 31 1655 (1975)

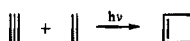
JOC 53 227 (1988) (intramolecular); 54 5148 (1989); 60 1381 (1995)

JACS 116 6622 (1994) (intramolecular)

SL 776 (1995) (intramolecular)



JACS 115 2239 (1993)



Ber 97 2942 (1964); 102 3974 (1969)

TL 3695 (1964); 3409 (1966); 27 2703 (1986) (intramolecular); 28 267 (1987); 33 3987 (1992) (intramolecular); 34 1709 (1993); 35 3883 (1994); 36 4189 (1995) (intramolecular)

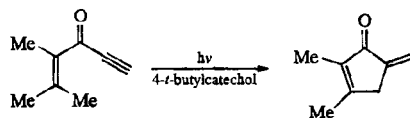
JOC 35 1237 (1970); 46 3389 (1981); 49 832 (1984) (intramolecular); 51 5232 (1986) (intramolecular); 55 1506, 4544 (1990); 57 6861 (1992); 59 1236 (1994)

J Heterocyclic Chem 8 1097 (1971)

JACS 93 782 (1971); 110 2157 (1988)

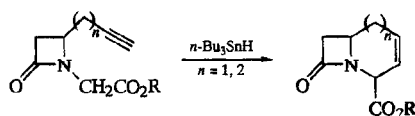
SL 789 (1991); 735 (1995)

Tetr 47 229 (1991)

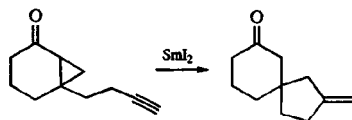


TL 33 2265 (1992)

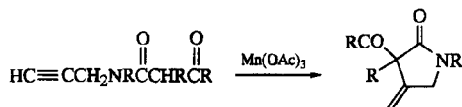
2.3. Free Radical



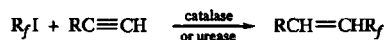
JOC 58 5581 (1993)



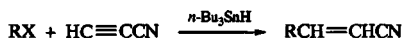
TL 32 6211, 6649 (1991)



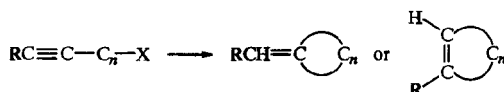
TL 30 4531 (1989)



JOC 53 2350 (1988)



JOC 53 1285 (1988)

X

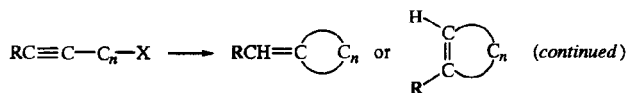
halogen




Reagent(s) $n\text{-Bu}_3\text{SnH}$ Ring Size

5

JOC 47 5382 (1982) (3-methylene tetrahydrofurans); 52 4943 (1987); 55 5823 (1990) (3-methylene dihydroindole); 57 2873 (3-methylene dihydroindole); 3085 (1992); 58 5709 (1993) (2-alkoxy 3-methylene tetrahydrofuran)
 JACS 105 3720 (1983) (3-alkylidene tetrahydrofurans); 107 1448 (1985) (serial cyclization); 110 1321, 4796 (1988) (3-methylene dihydroindoles); 111 6461 (3-methylene dihydroindole) (1989); 112 9401 (1990); 114 644 (1992)
 CL 1437 (1984) (3-methylene tetrahydrofurans)
 TL 26 6001 (1985) (3-methylene dihydrobenzofuran); 27 3715 (1986) (3-methylene tetrahydrofuran); 28 2009 (3-methylene tetrahydrofurans), 2887 (carbamapenam) (1987); 29 3335, 3691,

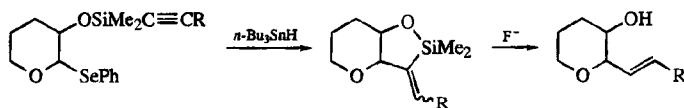
		4995, 6487 (all 3-methylene tetrahydrofurans), 6657 (oxindole) (1988); 30 7469 (3-alkylidene-4-alkanolactams and -4-alkanolides) (1989); 31 2193, 3555, 4445, 5397 (bicyclic lactams) (1990); 32 5873 (1991); 33 1893, 6025 (3-methylene tetrahydrofuran) (1992); 34 5615 (1993); 35 429, 1205 (both 3-methylene tetrahydrofurans), 3995, 8601 (serial cyclization), 8863 (serial cyclization) (1994); 36 4857 (1995)
		CC 587 (1987) (3-methylene tetrahydrofurans)
		SL 679 (1992) (3-methylene dihydroindole); 893, 923 (1995) (both 3-methylene tetrahydrofurans)
5, 6		TL 30 57 (1989) (3-alkylidene tetrahydrofuran, 4-alkylidene tetrahydropyran); 31 3745 (1990) (bicyclic ketones); 33 7857 (1992); 35 5853 (1994)
		JOC 57 6099 (1992)
6		JOC 44 546 (1979); 59 1234 (1994)
		JACS 114 644 (1992)
6, 7		TL 23 2505 (1982)
		JOC 48 1841 (1983)
		(both bicyclic β -lactams)
8		TL 34 8353 (1993)
10		TL 33 5653 (1992)
$n\text{-Bu}_3\text{SnH}$, Et_3B	5	JOC 57 6099 (1992)
$n\text{-Bu}_3\text{SnCl}$, NaBH_3CN	5	TL 28 5203, 6393 (1987); 35 7841 (1994) (all 3-methylene tetrahydrofurans)
Ph_3SnH	5	TL 32 2017 (1991)
		SL 58 (1991)
Ph_3SnH , electrolysis	5	TL 33 6495 (1992) (3-methylene tetrahydrofuran)
$(\text{Me}_3\text{Si})_3\text{SiH}$, Et_3B , O_2	5	TL 35 3995 (1994)
	5, 6	JOC 57 6099 (1992)
Co(I)	5	JOC 47 1775, 5382 (1982); 50 5875 (1985) (all 3-methylene tetrahydrofurans)
cat cobaloxime, NaBH_4	5	JOC 58 5709 (1993)
		TL 36 505 (1995)
(triphenyltin)cobaloxime, $h\nu$	5	(both 3-methylene tetrahydrofurans)
		JOC 60 6635 (1995) (3-methylene tetrahydrofuran)
vitamin B_{12} , reductant	5	Chimia 39 203 (1985)



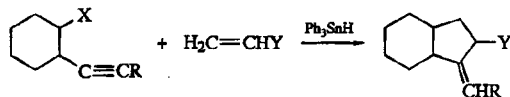
<u>X</u>	<u>Reagent(s)</u>	<u>Ring Size</u>	
	SnI_2	5	SL 805 (1991) TL 35 3995 (1994)
	Et_3N , hv	5	TL 35 8161 (1994); 36 2067 (1995) (both 3-methylene tetrahydrofurans)
NO_2	$n\text{-Bu}_3\text{SnH}$	5	CL 635 (1985) Tetr 41 4013 (1985) (both 3-methylene tetrahydrofurans)
$\text{O}_2\text{CC}_6\text{H}_4\text{CF}_3$	hv	5	JOC 52 5583 (1987)
OC(S)OPh	$n\text{-Bu}_3\text{SnH}$	5	JACS 112 4374 (1990)
OCS_2CH_3	$n\text{-Bu}_3\text{SnH}$	5	JOC 52 5583 (1987); 60 8179 (1995) TL 30 3561 (1989); 31 4931 (1990) (3-methylene tetrahydrofuran); 33 1539 (1992) (3-methylene tetrahydrofuran); 34 4313 (3-methylene tetrahydrofuran), 5615 (1993); 36 1487, 2661 (3-methylene tetrahydrofuran) (1995)
	$n\text{-Bu}_3\text{SnH}$	5, 6	JOC 49 1313 (1984)
	$n\text{-Bu}_3\text{SnH}$	5	SL 493 (1995)
	$(\text{Me}_3\text{Si})_3\text{SiH}$	5	SL 493 (1995)
SPh	$n\text{-Bu}_3\text{SnH}$	5	TL 31 759 (1990) (3-alkylidene pyrrolidine)
		5, 6	TL 23 4765 (1982) Tetr 41 3959 (1985) (pyrrolizidinones and indolizidinones)
		6	JOC 53 6022 (1988)
	Cy_3SnH	5	TL 29 57 (1988)
SePh	$n\text{-Bu}_3\text{SnH}$	5	TL 30 6307 (1989) SL 257 (1990); 285 (1992) (3-methylene tetrahydrofuran) JOC 56 5245 (1991); 58 7718 (1993) (3-methylene tetrahydrofuran)

Ph₃SnH6
5

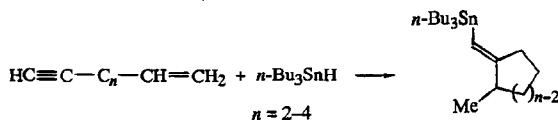
JOC 53 6022 (1988)
 CC 941, 1205 (1985); 878 (1986)
 JOC 52 1339, 4943 (1987); 55 1096
 (1990); 58 6857 (1993)
 JACS 116 11275 (1994)



JACS 113 7054 (1991)

X = Br, SePh; Y = CO₂Me, CN, SO₂Ph

CC 980 (1985)



JACS 109 2829 (1987)

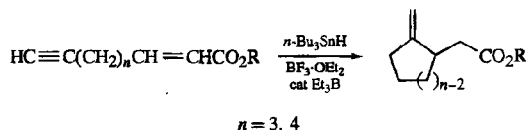
TL 28 1503 (1987); 29 1315, 6585 (1988); 30 827, 7115, 7219 (1989); 31 5039 (1990); 32 1799 (1991); 35
 7771 (1994); 36 7247, 7607 (1995)

Org Syn 66 75 (1987)

SL 766 (1990); 614 (1991)

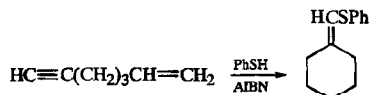
Org Syn Coll Vol 8 381 (1993)

JOC 60 3518 (1995)

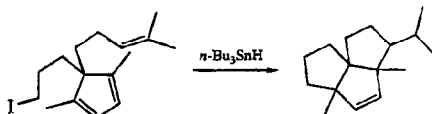


n = 3, 4

JACS 116 6455 (1994)



TL 28 1503 (1987)



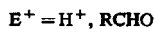
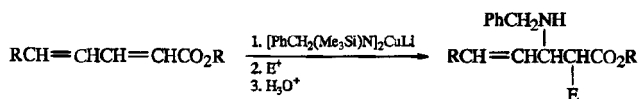
JACS 112 9272 (1990)



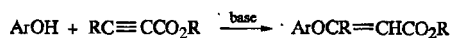
See page 655, Section 4.

2.4. Michael Additions

Review: SL 369 (1993) (intramolecular Michael and anti-Michael additions to carbon-carbon triple bonds)



JACS 114 5427 (1992)

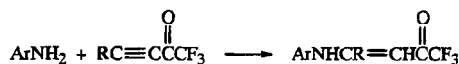


JACS 100 8202 (1978); 112 7032 (1990)

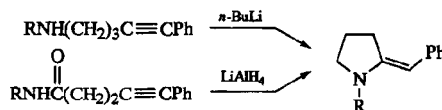
JOC 45 4813 (1980)



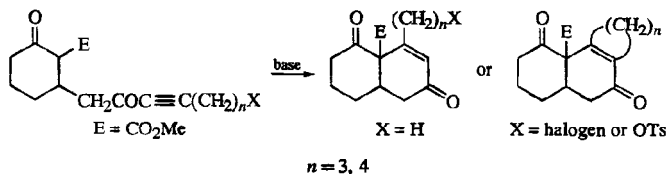
JACS 116 3389 (1994)



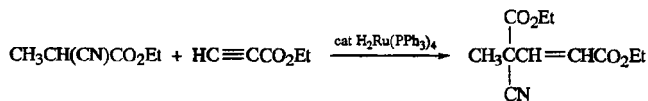
TL 31 2689 (1990)



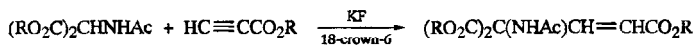
TL 31 5353 (1990)



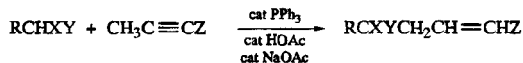
TL 27 5455 (1986); 28 3457 (1987); 29 3423 (1988)



JACS 111 5954 (1989)



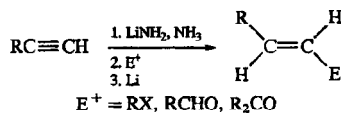
TL 29 6183 (1988)



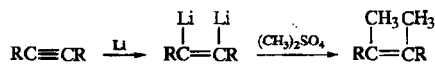
X, Y, Z = COR, CO₂R, CO₂R; CO₂R, CO₂R, CO₂R; CN, SO₂Ph,
CO₂R; SO₂Ph, SO₂Ph, CO₂R; CO₂R, CO₂R, CONR₂

JACS 116 3167 (1994)

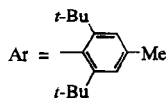
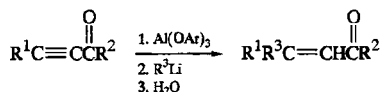
2.5. Organolithium Compounds



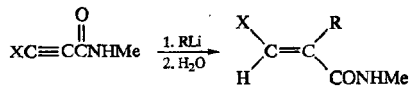
Syn 337 (1985)



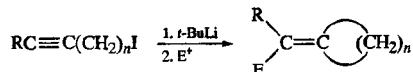
Angew Int 25 167 (1986)



SL 719 (1995)

X = Ph, SiMe₃

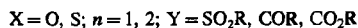
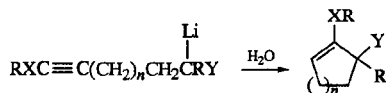
JACS 107 6740 (1985)



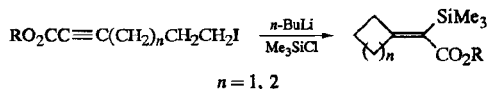
$n = 3\text{-}5$; $\text{E}^+ = \text{H}^+, \text{RX}, \text{epoxide}, \text{RCHO}, \text{R}_2\text{CO}, \text{DMF}, \text{CO}_2, \text{ClCO}_2\text{R}$

TL 30 3901 (1989); 31 493, 627 (1990)

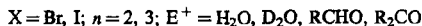
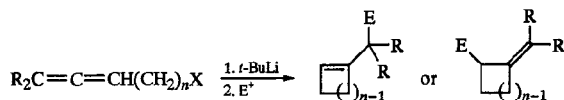
JACS 115 3080 (1993)



JACS 115 7023 (1993)



JOC 58 6833 (1993); 59 260 (1994)

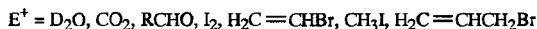
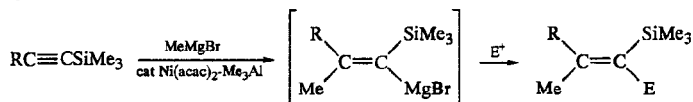


TL 33 5311 (1992)

JOC 57 2993 (1992)

2.6. Organomagnesium Compounds

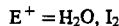
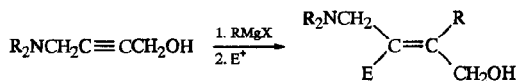
See also page 438, Section 2.14.



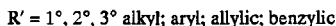
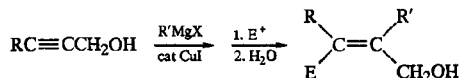
JACS 100 4624 (1978)

TL 1682 (1979)

Israel J Chem 24 108 (1984)

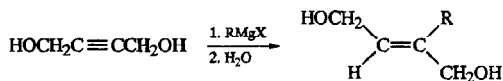


SL 505 (1990)



JOMC 168 1, 227, 233 (1979)

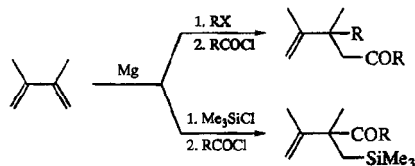
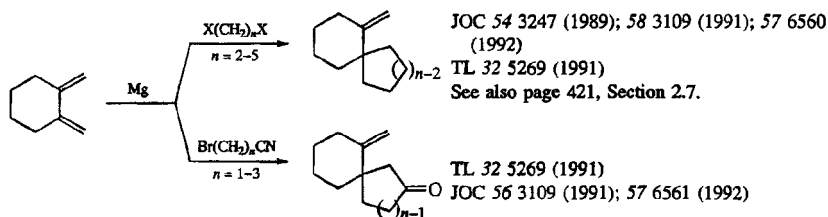
JOC 51 4080 (1986)



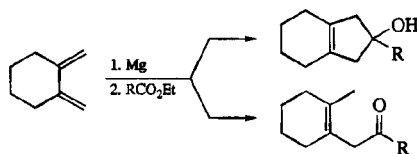
R = 1°, 2° alkyl; allyl; aryl; benzyl; vinylic

CL 765 (1984)

TL 29 2867 (1988)

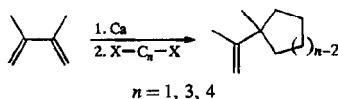


JOC 54 3247 (1989); 56 3109 (1991)



JACS 114 4415 (1992)

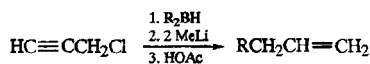
2.7. Organocalcium Compounds



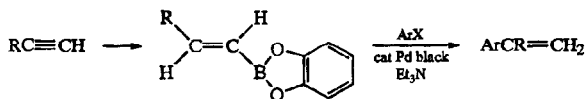
JOC 55 5045 (1990)

See also page 420, Section 2.6.

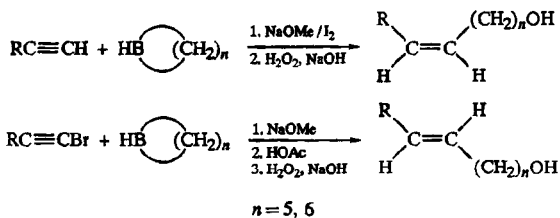
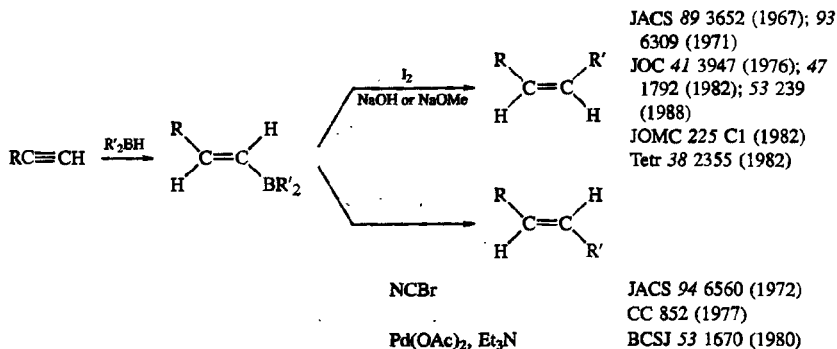
2.8. Organoboron Compounds



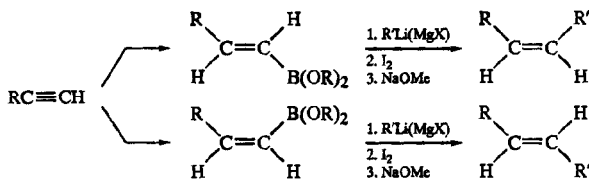
Syn 672 (1973)



JOMC 213 C53 (1981)

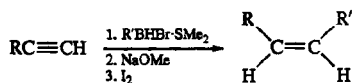


JOC 53 246 (1988)

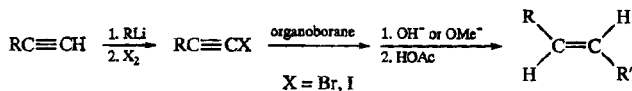


JOMC 110 25 (1976)

JOC 53 239 (1988)



JOC 47 171, 3806, 5407 (1982); 53 239 (1988)

Organoborane $\text{R}'_2\text{BH}$

JACS 89 5086 (1967); 94 4013 (1972)

Syn 555 (1972); 195 (1982)

JOC 47 754 (1982); 51 5270 (1986)

TL 23 2785 (1982)

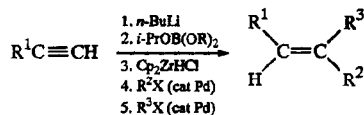
 $\text{R}'\text{BHBBr} \cdot \text{SMe}_2$

JOC 47 3808 (1982); 51 5270 (1986)

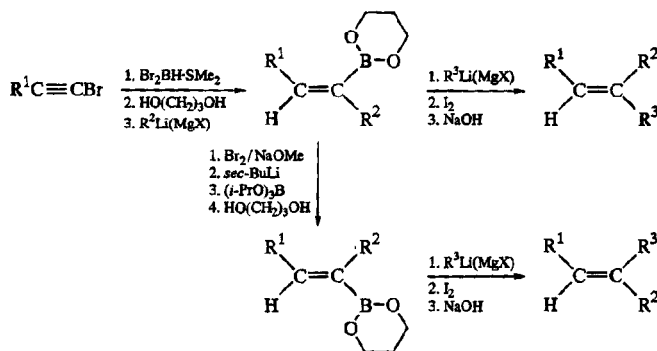
 $(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{BHR}'$

JOC 51 5270 (1986)

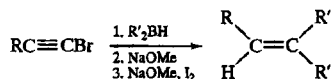
JACS 110 1529 (1988)

 $\text{R}^2 = \text{allylic, vinylic, aryl}; \text{R}^3 = \text{vinylic, aryl}$

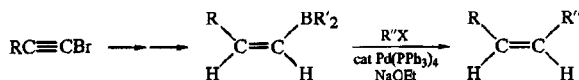
JACS 116 10302 (1994)



JOC 53 6009 (1998)

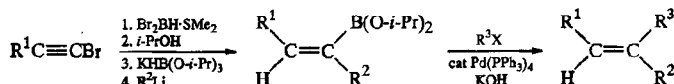


JOC 47 754 (1982)

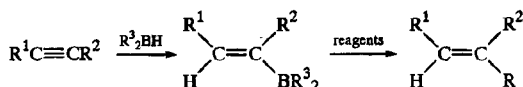


R' = aryl, vinylic

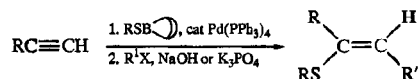
TL 27 3745 (1986)

R³ = allylic, aryl, vinylic

CL 1329 (1986)

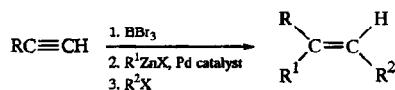
RReagents

$\text{CH}_2\text{CH}=\text{CH}_2$	NaOMe / CuBr·SMe ₂ / H ₂ C=CHCH ₂ Br MeLi / CuI / H ₂ C=CHCH ₂ Br MeCu / H ₂ C=CHCH ₂ Br Pd(OAc) ₂ , H ₂ C=CHCH ₂ Br cat Pd(PPh ₃) ₄ , NaOH, H ₂ C=CHCH ₂ Br	JOC 45 550 (1980) BCSJ 53 1471 (1980) JOC 45 1640 (1980) BCSJ 53 1670 (1980) TL 21 2865 (1980)
$\text{CH}_2\text{C}\equiv\text{CH}$	MeLi / CuI / HC≡CCH ₂ Br	BCSJ 53 1471 (1980)
CH_2Ar	cat Pd(PPh ₃) ₄ , NaOH, ArCH ₂ X (X = Cl, Br)	TL 21 2865 (1980) JOC 47 2117 (1982)
$\text{CH}_2\text{CO}_2\text{R}$	(Me ₂ SCH ₂ CO ₂ R)Br, NaH / NaOAc, H ₂ O ₂	JOC 57 4017 (1992)
Ar	cat Pd(PPh ₃) ₄ , NaOH, ArX (X = Br, I) cat Pd(PPh ₃) ₄ , NaOEt, ArX (X = Br, I)	JOC 47 2117 (1982) TL 32 43, 2311 (1991) CC 866 (1979)
$\text{CH}=\text{CHR}'$	—	See page 479, Section 3.4.
$\text{C}\equiv\text{CR}$	LiC≡CR / I ₂ , OH ⁻ NaOMe / CuCN or CuI / BrC≡CR cat Pd(PPh ₃) ₄ , BrC≡CR, base	CC 874 (1973) TL 27 539 (1986) See page 589, Section 2. See page 589, Section 2.



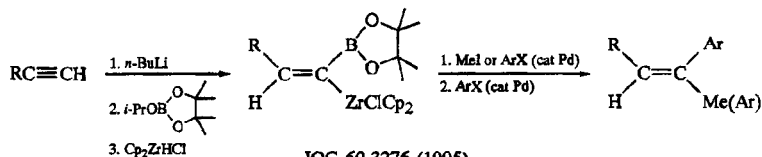
R' = aryl, alkynyl, vinylic, allylic, benzylic

JACS 115 7219 (1993)

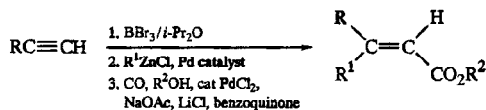


R¹ = alkyl, vinylic, aryl; R² = H⁺, benzylic, allylic, aryl, alkynyl, vinylic

TL 29 1811 (1988)

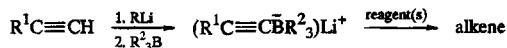


JOC 60 3276 (1995)

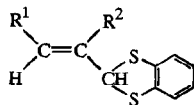
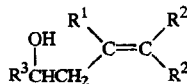
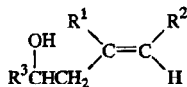
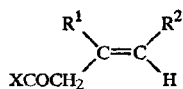
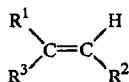
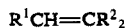
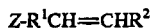


R¹ = alkyl, aryl, vinylic, alkynyl

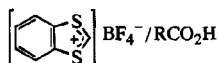
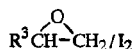
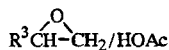
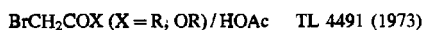
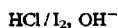
TL 30 6555 (1989)



Alkene



Reagent(s)



TL 2961 (1974); 28 1007 (1987)

Syn 376 (1975)

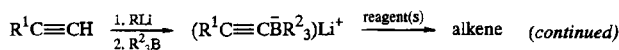
TL 1633 (1975); 28 1003, 1007 (1987)

TL 4491 (1973)

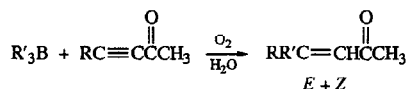
TL 2741 (1973)

TL 2741 (1973)

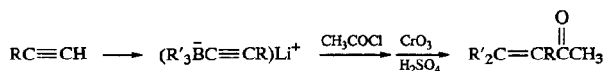
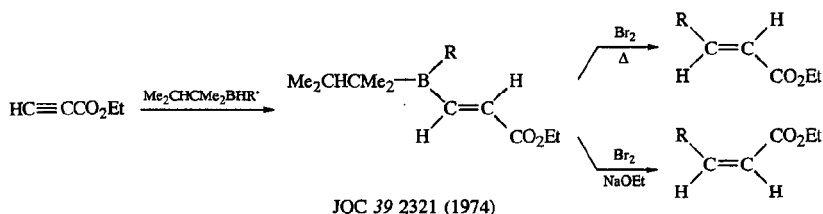
CC 164 (1981)

AlkeneReagent(s)

$R^1CH=CR^2CH_2CO_2Et$	$n\text{-Bu}_3\text{SnCl} / \text{Me}_2\text{S}^+\text{CHCO}_2\text{Et} / \text{H}_2\text{O}_2, \text{NaOAc}$	JOC 58 1949 (1993)
$R^2CH=CR^1CHR^3CHX\text{-CO}_2Et$	$R^3CH=CXCO_2Et$ ($X = \text{COCH}_3, \text{CO}_2\text{Et}$) / $i\text{-PrCO}_2\text{H}$	TL 22 797 (1981)



JACS 92 3503 (1970)



TL 795 (1973)

StereochemistryXReagents

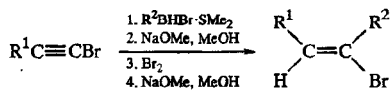
cis	Cl	CB/H ₂ O/Cl ₂ /Na ₂ SO ₃	TL 26 279 (1985)
	Br	(Sia) ₂ BH/Br ₂ /H ₂ O	JACS 89 4531 (1967)
		Br ₂ BH·SMe ₂ /Br ₂ /NaOH	JOC 54 6068 (1989)
		CB/Br ₂ , NaOMe	JOC 54 6068 (1989)
			JACS 95 6456 (1973)
trans	Br, I	RLi/X ₂ /C ₂ H ₅ BH/HOAc	JOC 54 6068 (1989)
	I	CB/py/I ₂	JACS 89 5086 (1967)
			JOC 54 6068 (1989)
	Cl	(Sia) ₂ BH/Cu ₂ Cl ₂ , H ₂ O, HMPA	JCS Perkin I 2725 (1992)
	Br	(Sia) ₂ BH/Cu ₂ Br ₂ , Cu(OAc) ₂ , H ₂ O, HMPA	JCS Perkin I 2725 (1992)
		(Sia) ₂ BH/Br ₂ /Δ	JACS 89 4531 (1967)
		Br ₂ BH·SMe ₂ /NaOH/I ₂	JOC 54 6068 (1989)
			JOC 45 389 (1980)

$\text{Br}_2\text{BH}\cdot\text{SMe}_2/\text{I}_2/\text{NaOH}$
 $\text{CB}/\text{I}_2, \text{NaOH}$

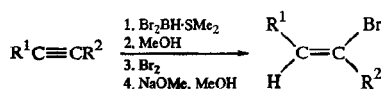
JOC 54 6068 (1989)
 JACS 95 5786 (1973)⁹
 CC 446 (1990)
 JOC 54 6068 (1989)
 Syn Commun 11 247
 (1981)

$\text{CB}/\text{py}/\text{I}_2$
 $\text{CB}/\text{ICl}, \text{NaOAc}$

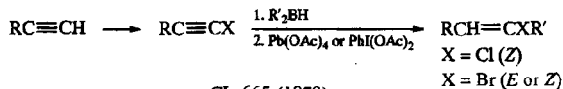
See also page 745, Section 13.



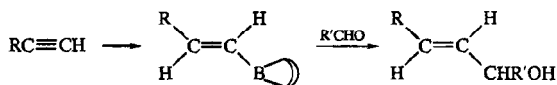
Syn 480 (1986)
 TL 29 21 (1988)



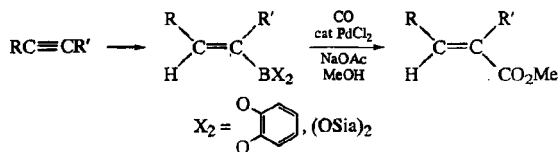
Syn 480 (1986)
 TL 29 21 (1988)



CL 665 (1978)
 BCSJ 53 1652 (1980)

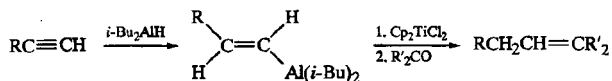


IOC 42 579 (1977)

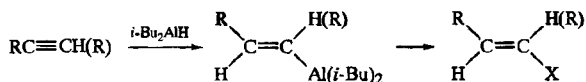







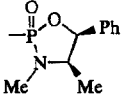
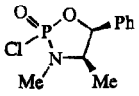
CL 879 (1981); 1329 (1986)

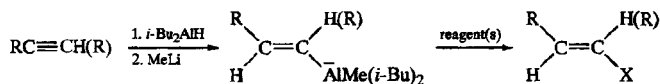
2.9. Organoaluminum Compounds





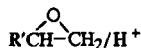
CL 429 (1982)



<u>X</u>	<u>Reagent(s)</u>	
Br	Br ₂	JACS 89 2753 (1967) JOC 58 4823 (1993)
I	I ₂	JACS 89 2753 (1967); 108 3403, 7791 (1986); 110 5383 (1988); 112 3096 (1991) TL 29 6243 (1988) JOC 58 4823, 7474 (1993)
CH ₂ OMe	ClCH ₂ OMe	Syn 816 (1976) TL 23 2087 (1982)
		JACS 112 9645 (1990) TL 32 2199 (1991)
CH ₂ N 	<i>i</i> -BuOCH ₂ N 	TL 21 3763 (1980)
Ar	ArX, cat Ni	See page 382, Section 20.
CH=CHR'	R'CH=CHX, cat Ni(O) R'CH=CHX, cat Pd(O)	See page 482, Section 3.5. See page 482, Section 3.5.
CHO	 / HCl	TL 33 2867 (1992)
CH ₂ CH ₂ COR	H ₂ C=CHCOR, (<i>n</i> -BuC≡C) ₂ Cu(CN)Li ₂	JOC 57 3178 (1992)
PO(OEt) ₂	ClPO(OEt) ₂	TL 36 6659 (1995)
		TL 36 6659 (1995)

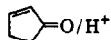


<u>X</u>	<u>Reagent(s)</u>	
R'	R'X	TL 1927 (1976)
CH ₂ N 	<i>i</i> -BuOCH ₂ N 	TL 21 3763 (1980)
CHR'OH	R'CHO/H ⁺	JACS 89 2754 (1967) TL 23 2087 (1982); 28 5129 (1987)

$\text{CH}_2\text{CHR}'\text{OH}$ 

Syn 632 (1975)

CC 17 (1976)



TL 4083 (1972)

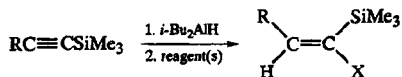
 CO_2H CO_2/H^+

JACS 89 2754 (1967)

CN

 $(\text{CN})_2$

JACS 90 7139 (1968)

XReagent(s)

H

 H_2O

JOC 36 3520 (1971)

Syn 803 (1980)

Cl, Br, I

NCS, Br_2 or I_2

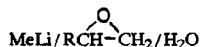
JOC 43 2739 (1978)

 R' $\text{MeLi}/\text{R}'\text{X}$ ($\text{R}' = \text{Me}, \text{allyl}$)

JOC 41 2214, 2215 (1976)

 CH_2OH $\text{H}_2\text{CO}/\text{H}_2\text{O}$

TL 28 3547 (1987)

 CH_2CHROH 

JACS 106 4192 (1984)

X E^+

R

RCHO

JOC 53 1037 (1988)

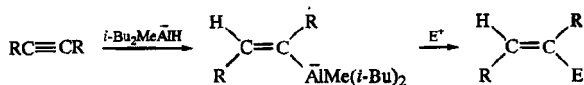
OR

allylic bromides

JOC 52 1624 (1987)

 $\text{RCHO}, \text{R}_2\text{CO} (\text{BF}_3 \cdot \text{OEt}_2)$

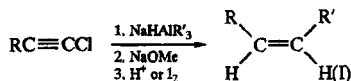
JOC 53 1037 (1988)

 E^+ $\text{CO}_2, \text{H}_2\text{CO}, \text{I}_2$

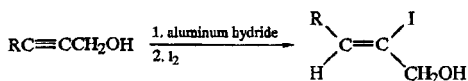
JACS 89 5085 (1967)

 $(\text{CN})_2$

JACS 90 7139 (1968)



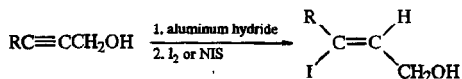
JOC 54 998 (1989)

Aluminum hydrideLiAlH₄, cat AlCl₃

JACS 89 4245 (1967); 91 4318 (1969)

n-BuLi / *i*-Bu₂AlH

JACS 92 6314 (1970)

Aluminum hydrideLiAlH₄, NaOCH₃

JACS 89 4245 (1967); 90 5618 (1968)

TL 1821 (1971); 28 5793 (1987)

LiAlH₂(OCH₂CH₂OCH₃)₂

TL 29 3899 (1988)

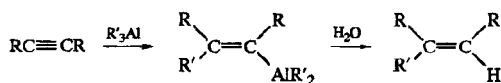
NaAlH₂(OCH₂CH₂OCH₃)₂

JOC 51 4316 (1986); 52 1236, 3860, 3883 (1987); 53 1616 (1988)

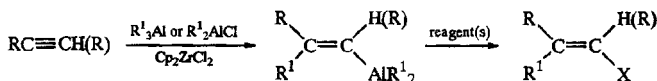
TL 28 723 (1987); 31 6137 (1990)

SL 279 (1991)

JACS 117 5776 (1995)



Ann 629 222 (1960)


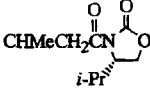
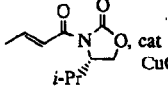


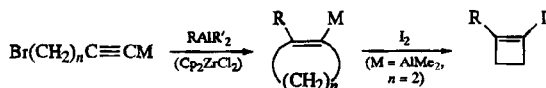
Review: Pure Appl Chem 53 2333 (1981)

XReagent(s)

H or D

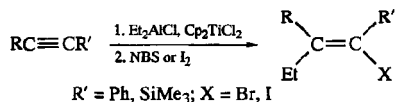
H₂O or D₂OJACS 100 2252 (1978); 103 4985 (1981); 107 6639 (1985)
JOC 46 4093 (1981)
TL 27 3311 (1986)I₂JACS 100 2252 (1978); 102 3298 (1980); 104 4708 (1984); 107 6639 (1985); 108 7791 (1986); 110 5383 (1988); 111 3336 (1989); 114 3926 (1992)
Syn 501 (1979)
JOC 46 4094 (1981); 51 2230 (1986); 58 832 (1993); 59 5803 (1994)

		TL 23 27 (1982); 33 2031 (1992); 36 5307 (1995) CL 293 (1982) CC 1237 (1986) JACS 117 8220 (1995)
R ²	R ² X, cat Pd(O) or Ni(O), ZnCl ₂ (R ² = aryl, vinylic, alkynyl, allylic, benzylic)	JACS 100 2254 (1978); 103 2882 (1981) TL 22 2715 (1981); 28 2221 (1987); 36 5307 (1995) Acct Chem Res 15 340 (1982) (review)
CH ₂ OH	<i>n</i> -BuLi / CH ₂ O	TL 2357 (1978) SL 279 (1991) JOC 59 4853 (1994)
CH ₂ OMe	<i>n</i> -BuLi / ClCH ₂ OMe	TL 2357 (1978)
CO ₂ H	<i>n</i> -BuLi / CO ₂ / H ⁺	TL 2357 (1978) JOC 46 4094 (1981)
CO ₂ Et	ClCO ₂ Et	TL 2357 (1978); 23 27 (1982) JOC 46 4094 (1981); 57 2794 (1992)
CH ₂ CHR ² OH	<i>n</i> -BuLi / H ₂ C  CHR ²	Syn 1034 (1980) JOC 45 5223 (1980) TL 30 1037 (1989)
CH ₂ CH ₂ COCH ₃	H ₂ C=CHCOCH ₃ H ₂ C=CHCOCH ₃ , cat CuCN·2LiCl (<i>n</i> -BuC≡C) ₂ Cu(CN)Li ₂ / H ₂ C=CHCOCH ₃	Pure Appl Chem 53 2333 (1981) JOC 56 5761 (1991) JOC 55 1425 (1990); 57 3178, 5071 (1992)
	 , cat CuCN·2LiCl	JOC 56 5761 (1991)
CH(N=CPh ₂)CO ₂ R	Ph ₂ C=NCH(OAc)CO ₂ R, cat Pd(PPh ₃) ₄	TL 35 9383 (1994)

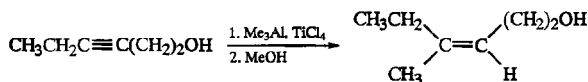


$n = 2, 4$; M = AlMe₂, SiMe₃; R = H, alkyl

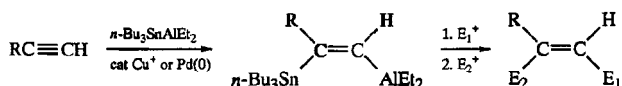
JACS 105 6344 (1983); 106 6105 (1984); 110 5383 (1988)



JOC 50 2121 (1985)



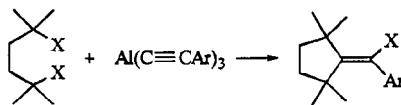
JOC 46 807 (1981); 50 2124 (1985)



$\text{E}_1^+ = \text{H}^+$; $n\text{-BuLi/RX}$ (MeI , $\text{H}_2\text{C}=\text{CHCH}_2\text{Br}$); RX ,
cat $\text{Pd}(0)$ ($\text{RX} = \text{H}_2\text{C}=\text{CHCH}_2\text{Br}$, PhCH_2Br , PhI)

$\text{E}_2^+ = \text{I}_2$ ($\text{E}_1 = \text{CH}_2\text{CH}=\text{CH}_2$); RX , cat $\text{Pd}(0)$ ($\text{RX} = \text{H}_2\text{C}=\text{CHCH}_2\text{Br}$,
 PhCH_2Br , vinylic iodide; $\text{E}_1 = \text{Me}$)

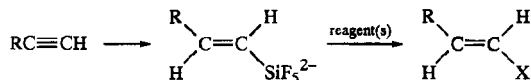
JOC 54 5064 (1989)

 $\text{X} = \text{Cl, Br}$

TL 32 521 (1991)

2.10. Organosilicon Compounds

Review: Syn 761 (1979) (electrophilic substitution of organosilicon compounds)

XReagent(s)

Cl, Br

 CuCl_2 or CuBr_2

Organomet 1 369 (1982)

Cl, Br, I

 Cl_2 , Br_2 , NBS or I_2

Organomet 1 355 (1982)

Ph

 PhI , Pd catalyst

Organomet 1 542 (1982)

 CO_2R CO , ROH, PdCl_2 , NaOAc

Organomet 1 542 (1982)

 $E\text{-CH}=\text{CHR}$

—

See page 484, Section 3.7.

$E\text{-CH=CHX}$ ($X = \text{CHO}$,
 CO_2R , CN)

$\text{H}_2\text{C=CHX}$, $\text{Pd}(\text{OAc})_2$

See page 484, Section 3.7.

$\text{CHR}^1\text{CR}^2=\text{CHR}^3$

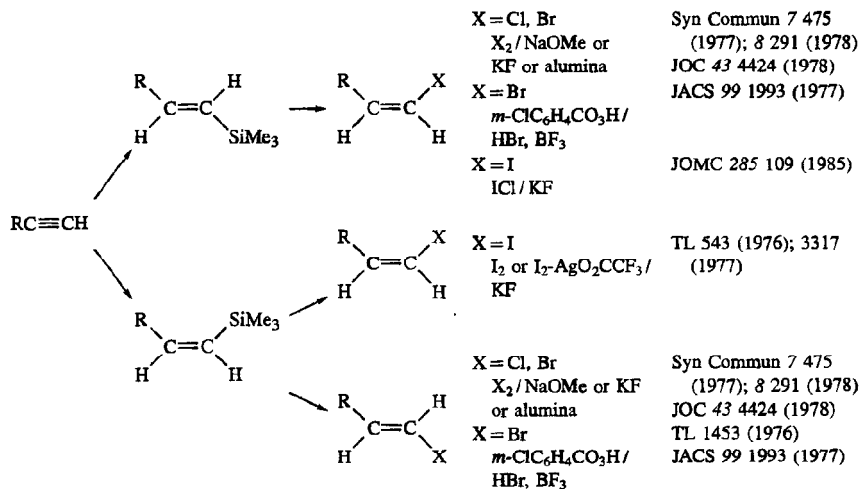
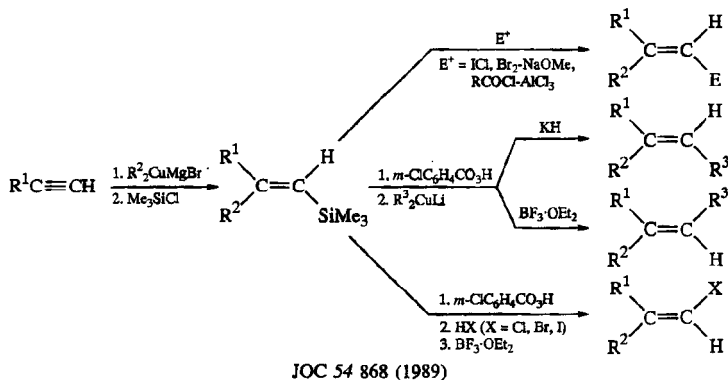
$\text{R}^1\text{CH=CR}^2\text{CHR}^3\text{X}$, $\text{Pd}(\text{OAc})_2$
($X = \text{Cl}$, Br , OTs)

See page 484, Section 3.7.

OR'

$\text{R}'\text{OH}$, O_2 , cat $\text{Cu}(\text{OAc})_2$

TL 21 4105 (1980)



Reviews:

Syn 761 (1979) (halogenation of organosilanes)
TL 27 883 (1986) (I_2 , AlCl_3 or SnCl_4 -variable stereochemistry)
JOC 52 1100 (1987) (stereochemistry of halogenation)
See also page 745, Section 13.



COR

$n\text{-Bu}_3\text{SnH} / n\text{-BuLi} /$
 $n\text{-C}_3\text{H}_7\text{C}\equiv\text{CCu} /$
 cyclopentenone / H_2O

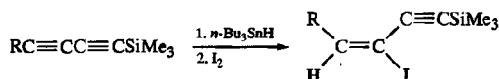
 $n\text{-Bu}_3\text{SnH} / \text{RCOCl}$, cat Pd

JOC 40 2265 (1975); 43 3450
 (1978)
 TL 4705 (1976)

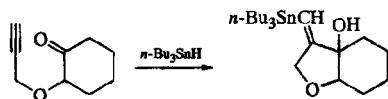
See page 1389, Section 2.6.

See also the appropriate function group X.

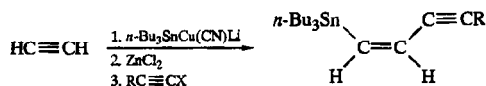
For the Pd-catalyzed hydrostannation of alkynes, see TL 29 619 (1988).



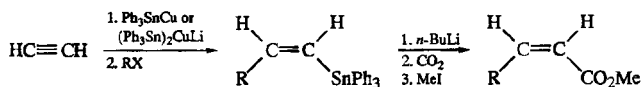
TL 32 3329 (1991)



See page 1176, Section 2.2.



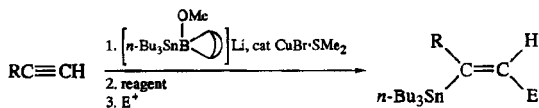
TL 32 6085 (1991)



TL 23 2797 (1982)

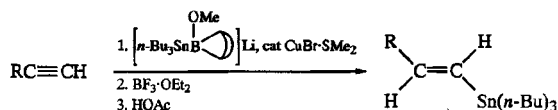


Can J Chem 66 1425 (1988)
 JACS 112 9397 (1990)

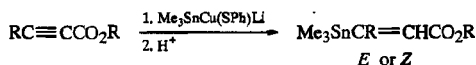
**Reagent**CuBr·SMe₂Pd(PPh₃)₄"Pd(PPh₃)₂"**E⁺**HCl, H₂C=CHCH₂Br, enone
(1,4-addition, BF₃·OEt₂)H₂C=CHCH₂Br

PhI

TL 29 261 (1988)



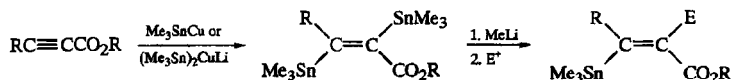
TL 29 261 (1988)



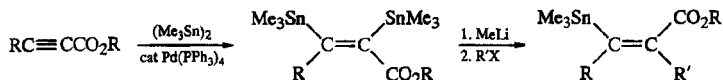
JOC 45 4263 (1980)

TL 22 4905 (1981)

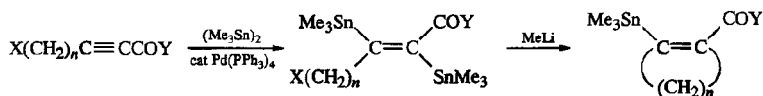
Organomet 2 184 (1983)

 $\text{E}^+ = \text{RX}$ (1° alkyl, allylic, benzylic), R_2CO

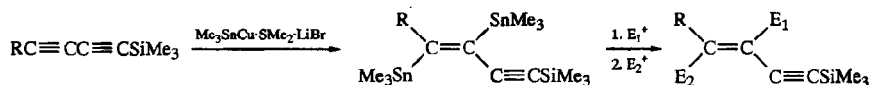
JOC 47 1602 (1982)



JOC 52 4421 (1987)

 $\text{X} = \text{halogen}; \text{Y} = \text{OR}, \text{NR}_2; n = 3-5$

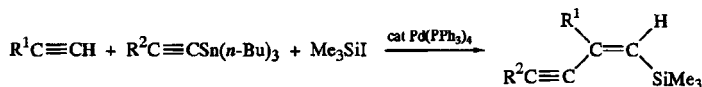
CC 626 (1986)

 E_1^+ $\text{MeLi}/\text{R}'\text{X}$ E_2^+ $\text{MeLi}/\text{R}^2\text{X}$

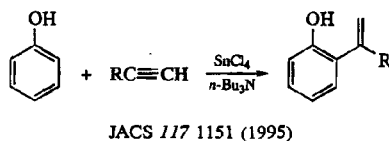
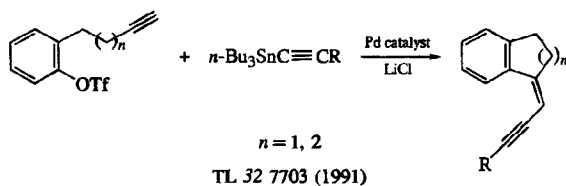
JACS 109 6409 (1987)

 MeLi/MeOH or $\text{R}'\text{X}$ I_2

TL 32 3329 (1991)

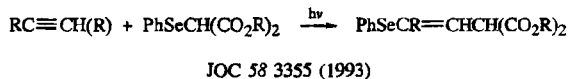
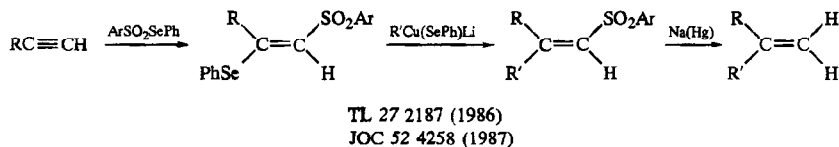


JACS 113 7778 (1991)



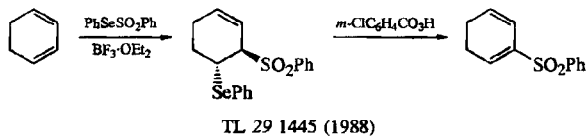
2.12. Organosulfur and -selenium Compounds

For the reduction of sulfides and selenides to free radicals and subsequent cyclization onto alkynes, see page 413, Section 2.3.

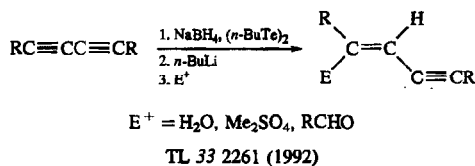
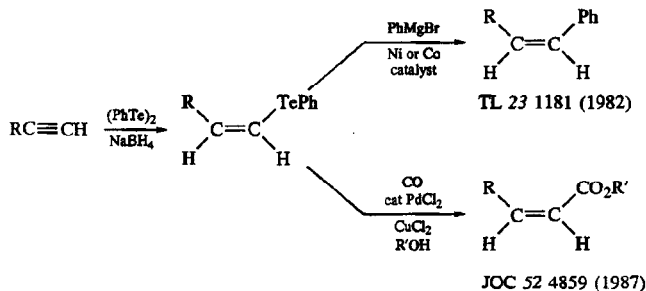


<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
O ₂ SC ₆ H ₄ CH ₃ - <i>p</i>	SePh	TsSePh	JOC 54 4146 (1989); 55 4595 (1990); 56 454 (1991)
O ₃ SAr	SePh	PhSeO ₃ SAr	TL 31 1957 (1990) JOC 56 2781 (1991)
SePh	SePh	(PhSe) ₂ , hv	JOC 56 5721 (1991)

For X and/or Y equals halogen, see page 655, Section 4.

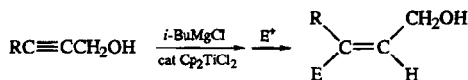
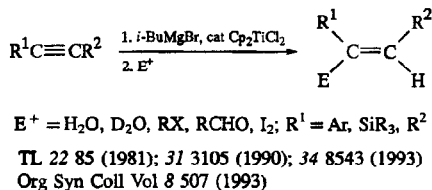
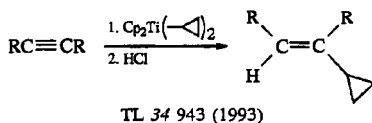
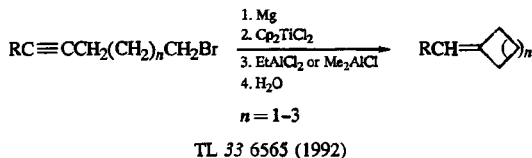


2.13. Organotellurium Compounds



2.14. Organotitanium Compounds

See also page 427, Section 2.9.



E^+

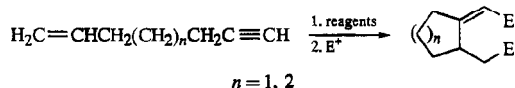
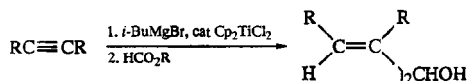
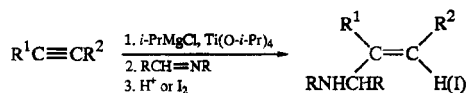
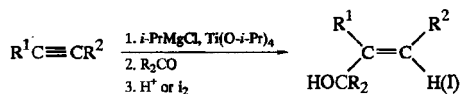
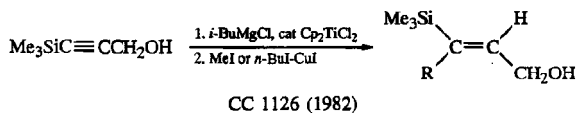
MeI

CC 718 (1981)

 CO_2/H^+

JOC 52 3860 (1987)

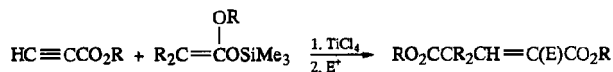
TL 29 2867 (1988)

Reagents E^+ Cp_2TiCl_2 , Na(Hg), Ph_2PMe H^+

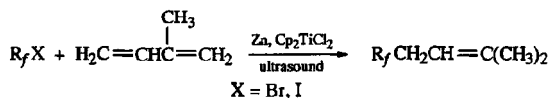
JACS 110 7128 (1988)

 $Ti(O-i-Pr)_4$, $i\text{-PrMgCl}$ HCl, DCl, I_2

TL 36 4261 (1995)

 $E^+ = H_2O, NCS, NBS, PhSeCl, RCHO, R_2CO$

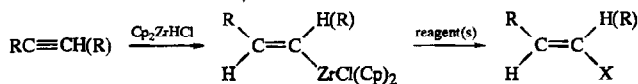
JOC 57 6890 (1992)


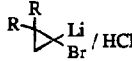




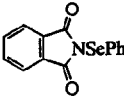
JACS 107 5186 (1985)

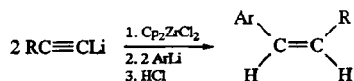
2.15. Organozirconium Compounds

See also page 421, Section 2.8, and page 427, Section 2.9.

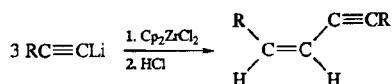


<u>X</u>	<u>Reagent(s)</u>	
H(D)	H ₂ O (D ₂ O)	TL 31 7257 (1990); 35 4669 (1994) JOC 56 2590 (1991)
R	2 MeMgCl/ThCu(CN)Li/ROTF	TL 32 5647 (1991)
PhCH ₂	2 MeMgCl/ThCu(CN)Li/PhCH ₂ Br	TL 32 5647 (1991)
	 /HCl	JACS 111 3089 (1989)
Ar	ArI, cat Ni(PPh ₃) ₄	JACS 99 3168 (1977) JOC 52 3319 (1987)
CH=CHR ¹	R ¹ CH=CHX, cat Pd(O)	See page 494, Section 3.13.
CH(R)=CHR	CuCl	See page 494, Section 3.13.
CH ₂ CH=CH ₂	—	See page 494, Section 3.13.
C≡CCH ₃	LiC≡CCH ₂ Cl/HCl	JACS 111 3089 (1989)
CH ₂ CH=CH ₂	ClCH ₂ CH=CH ₂ , ZnCl ₂	JOC 60 6260 (1995)
CH(OH)R	RCHO, cat AgClO ₄	TL 33 5965, 5969 (1992); 35 4669 (1994)
	R ₂ Zn (R = Me, Et)/RCHO	TL 35 5197 (1994)
CH(OH)CH ₂ R	 , cat AgClO ₄	JOC 58 825 (1993) TL 35 4669 (1994)
CH ₂ CH(OH)R	2 MeMgCl/ThCu(CN)Li/  CHR, (BF ₃ ·OEt ₂)	TL 32 5647 (1991)
CH ₂ CH ₂ COR ¹	H ₂ C=CHCOR ¹ , cat Ni(acac) ₂ H ₂ C=CHCOR ¹ , cat Ni(acac) ₂ - <i>i</i> -Bu ₂ AlH H ₂ C=CHCOR ¹ , CuOTf, LiI	JACS 99 8045 (1977); 102 1333 (1980) TL 4381 (1978) TL 1303 (1977)
CHO	RNC/H ₃ O ⁺	TL 29 1631 (1988)
CO ₂ H	<i>n</i> -BuTeBr/ <i>n</i> -BuLi/CO ₂ /H ₃ O ⁺	TL 36 7623 (1995)
CO ₂ R	<i>n</i> -BuTeBr/ <i>n</i> -BuLi/ClCO ₂ Et	TL 36 7623 (1995)
CN	RNC (R = <i>t</i> -Bu, SiMe ₃)/I ₂	TL 28 295 (1987)
Cl	NCS	JACS 97 679 (1975)

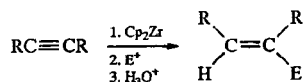
Br	Br ₂ NBS	JOC 57 5060 (1992) JACS 97 679 (1975); 108 5559 (1986); 112 5583 (1990) TL 31 7257 (1990); 35 4669 (1994) JOC 57 5071 (1992); 58 6779 (1993)
I	I ₂ NIS	JACS 97 679 (1975); 109 2138 (1987) Agric Biol Chem 46 717 (1982) TL 29 1509 (1988); 31 7257 (1990); 33 3715 (1992); 36 3763 (1995) JOC 56 2590, 2883 (1991); 57 3203 (1992) TL 35 4669 (1994)
SePh		JOC 52 2334 (1987)
TePh	PhTeI	TL 36 1503 (1995)
Te(<i>n</i> -Bu)	<i>n</i> -BuTeBr	TL 36 7623 (1995)



JACS 113 1440 (1991)



JACS 113 1440 (1991)

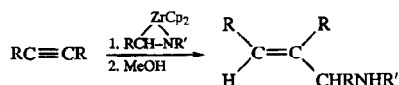
E⁺RCHO, R₂COCL 623 (1987)
JACS 109 2544 (1987); 113 1440 (1991)
TL 30 3495 (1989)

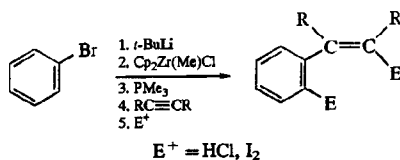
RCN

JACS 111 3336 (1989)

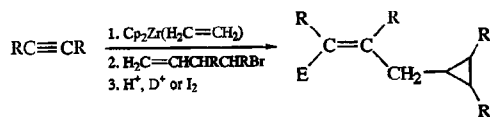
RNCO

TL 30 3495 (1989)

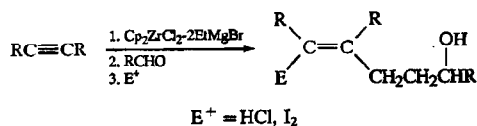
JACS 111 4486, 4495 (1989); 113 2321 (1991) (chiral)
SL 271 (1990); 143 (1992)
TL 32 5465 (1991); 35 1445, 2431 (1994)



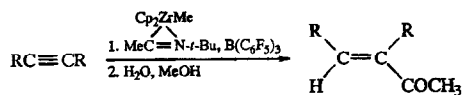
TL 31 5563 (1990)



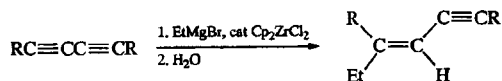
TL 34 6571 (1993)



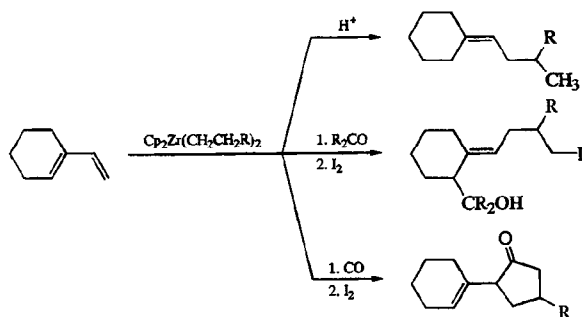
TL 35 695 (1994)



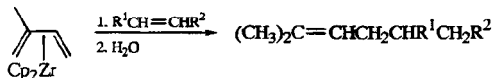
JOC 58 5595 (1993)



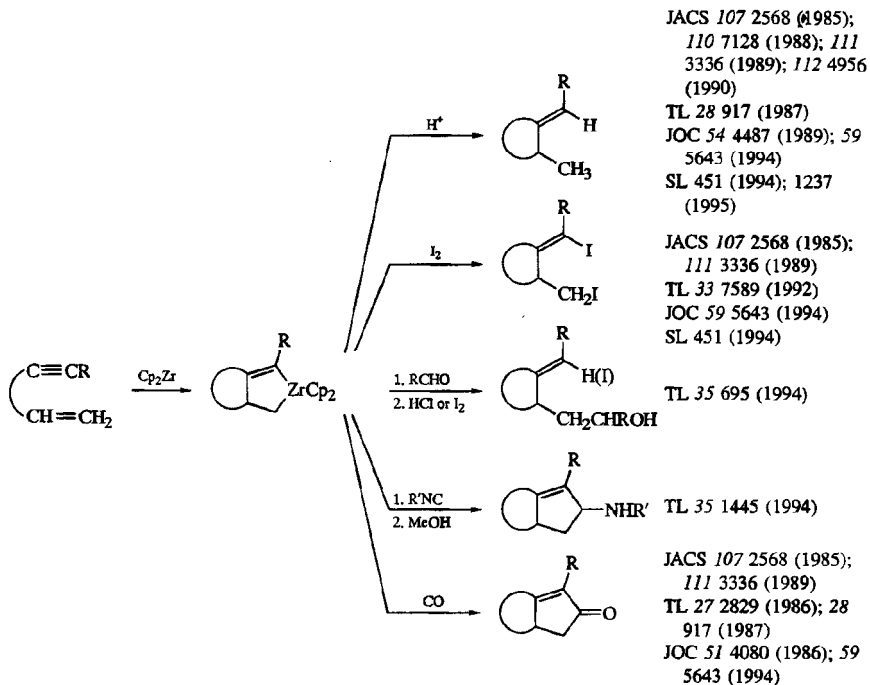
TL 34 8301 (1993)



JOC 54 6014 (1989)

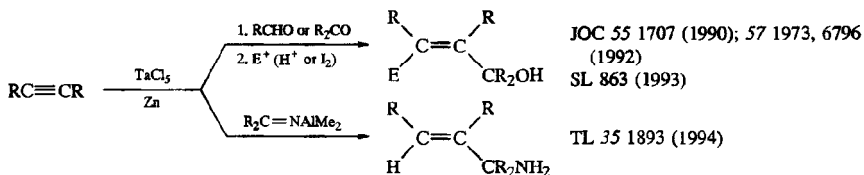


CL 719 (1981)

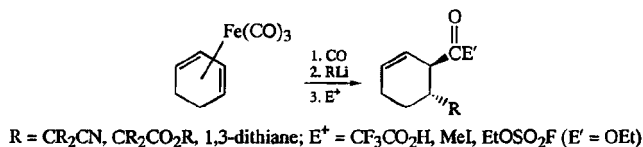
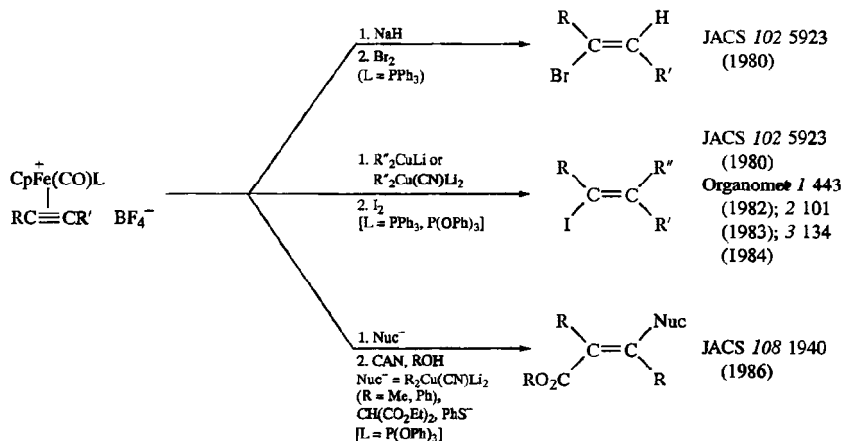


Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 9.5, p 1163

2.16. Organotantalum Compounds

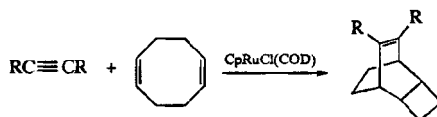


2.19. Organoirron Compounds

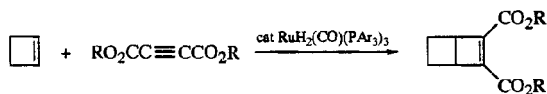


JACS 105 2497 (1983)

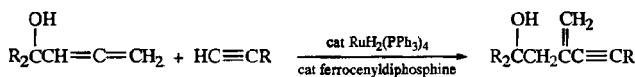
2.20. Organoruthenium Compounds



JACS 115 8831 (1993)

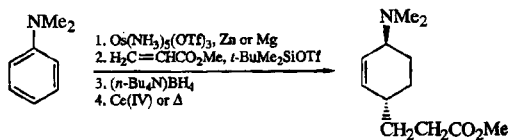


JOC 44 4492 (1979); 60 4051 (1995) (both norbornenes)
 TL 35 7639 (1994)



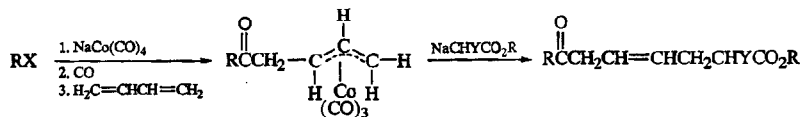
SL 1181 (1995)

2.21. Organosmium Compounds

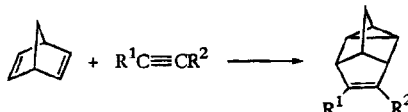


JACS 115 8857 (1993)

2.22. Organocobalt Compounds



JACS 104 4917 (1982)

CatalystCo(acac)₃, Et₂AlCl, phosphine

CC 636, 638 (1978)

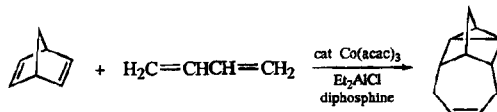
Ann NY Acad Sci 333 273 (1980)

JACS 112 5627 (1990) (chiral); 117 6863 (1995)

JOC 57 8 (1991) (intramolecular)

CoI₂, Zn, PPh₃

JOC 60 1868 (1995)



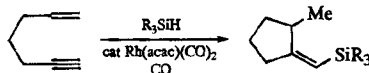
JOC 36 1443 (1971); 58 4513 (1993) (chiral)

Ann NY Acad Sci 333 273 (1990)

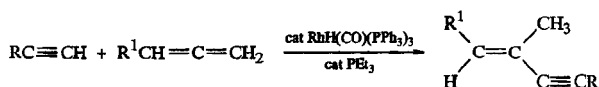
JACS 117 6863 (1995)

2.23. Organorhodium Compounds

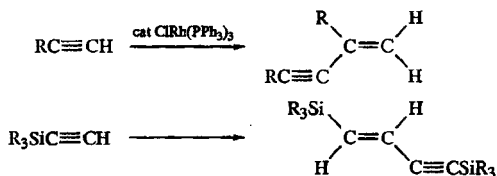
See also page 461, Section 2.32.



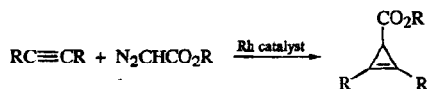
JACS 114 6580 (1992)



TL 35 5689 (1994)



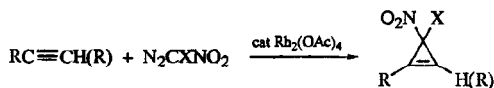
IOC 55 3277 (1990)



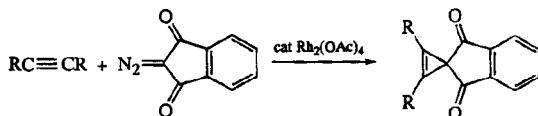
TL 1239 (1978); 33 3473 (1992)

JACS 114 2755 (1992) (chiral); 115 9968 (1993) (chiral); 116 8492 (1994) (chiral)

SL 505 (1992); 151 (1993)

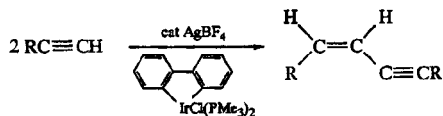
X = H, CO₂Et, CN

IOC 56 2258 (1991)



IOC 53 2699 (1988)

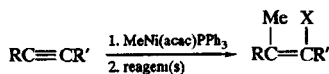
2.24. Organoiridium Compounds



TL 33 7119 (1992)

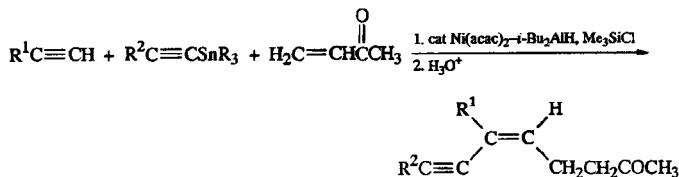
2.25. Organonickel Compounds

See also page 420, Section 2.6, and page 427, Section 2.9.

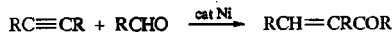


X	Reagent(s)
H	TsOH or LiAlH_4
Me	Me_3Al or MeLi
I	I_2
CO_2Me	CO , MeOH

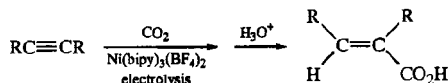
JACS 103 3002 (1981)



JACS 116 5975 (1994)

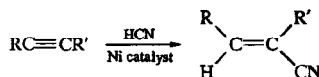


See page 1378, Section 22.



JACS 113 8447 (1991)

JOC 58 2578 (1993)



CC 1231 (1982); 4, 1509 (1985)

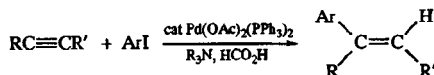
Austral J Chem 36 1975 (1983)

JOMC 285 375 (1985)

TL 29 1983 (1988)

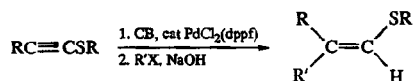
2.26. Organopalladium Compounds

See also page 421, Section 2.8; page 427, Section 2.9; page 432, Section 2.10; page 434, Section 2.11; and page 460, Section 2.30.



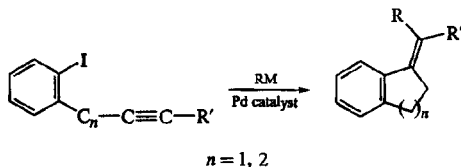
TL 25 3137 (1984) ($\text{R}=\text{R}'=\text{Ph}$); 27 6397 (1986) ($\text{R}'=\text{SiMe}_3$); 29 4325 (1988) (intramolecular); 34 835 (1993) (intramolecular)

Tetr 41 5121 (1985) ($\text{R}=\text{Ar}$, $\text{R}'=\text{CR}_2\text{OH}$)



R' = aryl, vinylic, alkynyl

JOC 58 5351 (1993)

 $n = 1, 2$

RM

$n\text{-Bu}_3\text{SnR}$ ($\text{R} = \text{aryl, vinylic, allylic, alkynyl}$)

TL 29 5565 (1988); 31 4393 (1990)

 AlPh_3

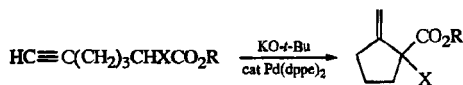
TL 31 4393 (1990)

$$\text{RCH}=\text{CHZnX}$$

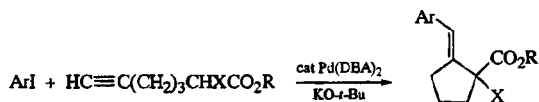
TL 31 4393 (1990)

 PhZnX

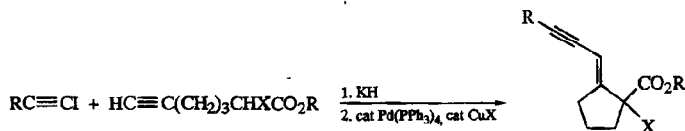
JOC 55 4846 (1990)


$$X = \text{COR, CO}_2\text{R}$$

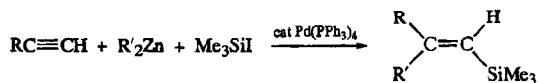
TL 32 1645 (1991)


$$X = \text{COR}, \text{CO}_2\text{R}, \text{SO}_2\text{Ar}$$

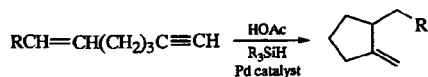
TL 31 5147 (1990)


$$X = \text{COR}, \text{CO}_2\text{R}, \text{CN}, \text{SO}_2\text{R}$$

TL 32 6541 (1991)

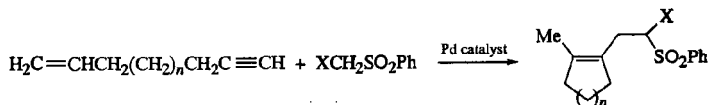


JOC 60 1834 (1995)

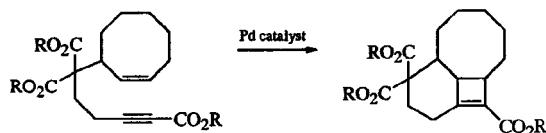


JACS 109 3161 (1987); 112 4956 (1990)

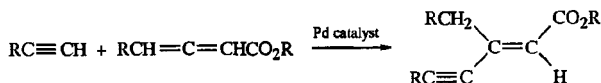
TL 29 1231 (1988)

 $n = 1, 2; \text{X} = \text{COMe}, \text{SO}_2\text{Ph}$

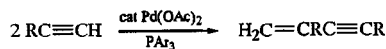
TL 35 1361 (1994)



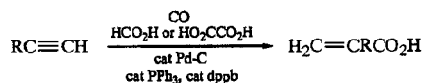
JACS 115 5294 (1993)



JACS 112 2816 (1990)

 $\text{X} = \text{CO}_2\text{Me}, \text{SO}_2\text{Ph}$

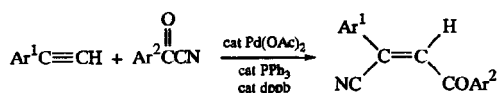
JACS 109 3486 (1987); 111 8745 (1989) (intramolecular, macrocycles)



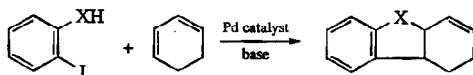
JOC 58 4739 (1993)



CC 1231 (1982)



JOC 59 2679 (1994)

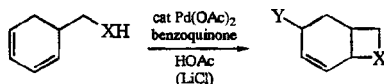


X = O, CH₂O, NAc, NTs, CH₂NTs, C(CO₂R)₂, CHCO₂R, CH₂C(CO₂R)₂,
CH₂C(SPh)CO₂R, CH₂C(CN)CO₂R, CH₂CHNO₂, COCH₂

JACS 112 5882 (1990)

JOC 55 3447 (1990); 60 482 (1995)

SL 465 (1995)



X

CH₂O

CO₂

CH₂NCO₂R

Y

Cl, OR, OAc

Cl, OAc

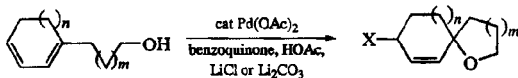
Cl

JACS 114 6374 (1992)

TL 30 137 (1989)

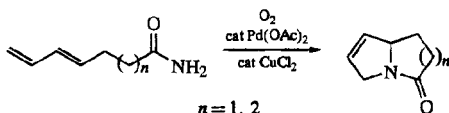
JOC 58 5445 (1993)

JOC 56 2988 (1991)



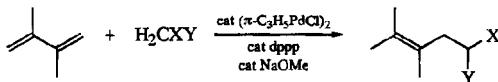
n = 1, 2; m = 1, 2; X = Cl, OAc

JOC 56 2274 (1991)



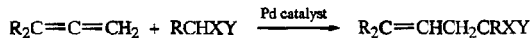
n = 1, 2

JACS 114 8696 (1992)



X = PhSO₂, COCH₃; Y = PhSO₂, COCH₃, CO₂CH₃

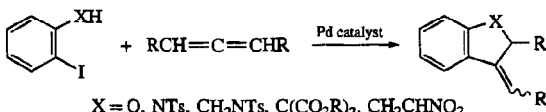
TL 33 1831 (1992)



X, Y = CO₂R, CO₂R; CO₂R, CN; CN, CN; SO₂Ar, SO₂Ar

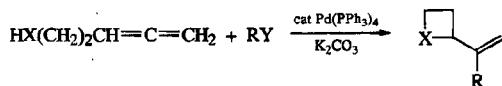
JACS 116 6019 (1994); 117 5156 (1995)

SL 969 (1995)



X = O, NTs, CH₂NTs, C(CO₂R)₂, CH₂CHNO₂

JOC 56 2615 (1991)



X

CH₂O

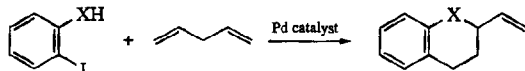
SL 88 (1993)

CO₂

SL 88 (1993)

CH₂NR, CH₂NTs, CH₂NBoc

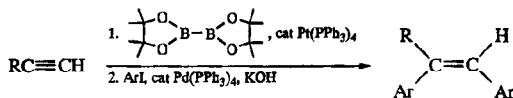
SL 85 (1993)



JOC 58 4509 (1993)

2.27. Organopalladium and -platinum Compounds

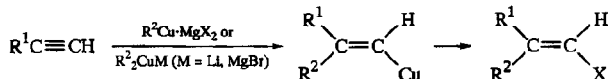
See also page 1690, Section 3.



JACS 115 11018 (1993)

2.28. Organocopper Compounds

See also page 420, Section 2.6; page 421, Section 2.8; page 434, Section 2.11; and page 445, Section 2.19.



Reviews:

Pure Appl Chem 50 709 (1978)

Syn 841 (1981)

Tetr 40 641 (1984)

"Current Trends in Organic Synthesis. Proceedings of the 4th International Conference on Organic Synthesis," Ed. H. Nozaki, Pergamon, New York (1982), pp 291-302

Org Syn Coll Vol 7 236 (1990)

Formation of the vinylcopper reagent:

TL 2583 (1971); 3461 (1976); 2023 (1977); 1363 (1978); 29 4313 (1988)

BSCF 1656 (1974)

Rec Trav Chim 95 299, 304 (1976); IOO 98, 249 (1981)



JOC 44 3888 (1979)

JOMC 177 293 (1979); 215 CI (1981)

Use of functionally-substituted alkynes:

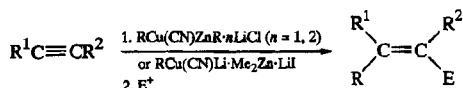
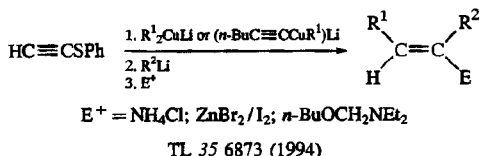
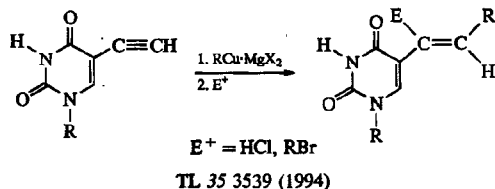
TL 2583 (1971); 2313 (1976); 24 5077 (1983); 28 2363 (1987)
 JOMC 57 C99 (1973); 144 13 (1983)
 J Mol Catal I 43 (1975/76)
 BSCF 693 (1977)
 Rec Trav Chim 100 337 (1981)

<u>X</u>	<u>Reagent(s)</u>	
H(D)	H ⁺ (D ⁺)	TL 2583 (1971); 2023 (1977); 1363 (1978); 23 5155 (1978); 24 5077 (1983); 29 4313 (1988) JOMC 77 269 (1974) BSCF 1656 (1974) Rec Trav Chim 95 299, 304 (1976); 100 98, 337 (1981) JOC 44 3888 (1979); 52 5419 (1987); 58 5316 (1993) Syn Commun 11 157 (1981) J Chem Res (S) 354 (1981) JACS 111 6717 (1989)
Cl	NCS, HMPA	TL 2023, 3545 (1977) Rec Trav Chim 96 168 (1977)
Br	HgBr ₂ /Br ₂ , py NBS, HMPA BrCN	Syn 803 (1974) TL 2023, 3545 (1977) Rec Trav Chim 96 168 (1977) Rec Trav Chim 96 168 (1977)
I	I ₂ ICN	TL 2583 (1971); 3461 (1976); 23 5155 (1982); 29 6243 (1988); 36 2765 (1995) JOMC 77 269 (1974); 177 293 (1979) Rec Trav Chim 96 168 (1977) JOC 43 1279 (1978); 52 1381 (1987) J Chem Res (S) 354 (1981) JACS 106 6105 (1984); 110 5383 (1988) Org Syn 62 1 (1984) Org Syn Coll Vol 7 290 (1990) Rec Trav Chim 96 168 (1977) JOC 52 4885 (1987)
R ³	R ³ X, HMPA, P(OR ⁴) ₃ (R ³ = 1° alkyl, allylic, benzylic, R ³ OCHR ⁶ X; X = Cl, Br, I; R ⁴ = Me, Et)	TL 2583 (1971); 1363, 3125 (1978); 1433 (1980); 23 3587, 5155 (1982) JOMC 40 C49 (1972); 77 269 (1974) Syn 826 (1979) JOC 44 1345, 3888 (1979) Rec Trav Chim 100 249 (1981) J Chem Res (S) 354 (1981) Org Syn 64 1 (1986)

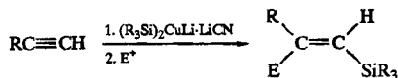
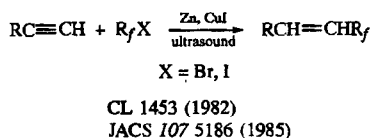
X	Reagent(s)	
Ar	ArI, ZnBr ₂ , cat Pd(PPh ₃) ₄	TL 22 3851 (1981) BSCF II 321 (1983)
CHR ³ OMe	R ³ CH(OMe) ₂ , BF ₃ ·OEt ₂	TL 25 3075 (1984)
CH ₂ OH	H ₂ CO/H ⁺	Tetr 36 1961 (1980)
CHR ³ OH	R ³ CHO, BF ₃ ·OEt ₂ R ³ CHXO(CH ₂) ₂ Cl (X = Cl, Br)/ n-BuLi/H ⁺	TL 26 2731 (1985) TL 2407 (1973) JOMC 77 269 (1974)
CHR ³ SR ⁴	ClCHR ³ SR ⁴	JOMC 77 269 (1974) Syn 43 (1984)
CH ₂ NMe ₂	(Me ₂ N=CH ₂)I ⁻	BSCF II 377 (1984)
CHR ⁴ NR ³ ₂	R ³ SCHR ⁴ NR ³ ₂ R ³ OCHR ⁴ NR ³ ₂	TL 21 3763 (1980); 23 5155 (1982) BSCF II 377 (1984) BSCF II 377 (1984)
CH ₂ N(CH ₃)CHO	ClCH ₂ N(CH ₃)CHO	Syn 40 (1984)
		Syn 40 (1984)
COR ³	R ³ COCl, HMPA or cat Pd(PPh ₃) ₄	TL 1363 (1978); 24 5081 (1983) JOC 44 3888 (1979) Pure Appl Chem 56 91 (1984) Tetr 42 1369 (1986)
CO ₂ H	CO ₂ , HMPA, cat P(OEt) ₃ /H ⁺	JOMC 54 C53 (1973); 77 281 (1974); 144 13 (1978) TL 3461 (1976); 23 5155 (1982) JOC 44 1345 (1979) Tetr 36 1961 (1980) Rec Trav Chim 100 249 (1981)
CS ₂ CH ₃	CS ₂ /CH ₃ I	Syn 432 (1979)
CONHPh	PhNCO/H ⁺	JOMC 54 C53 (1973); 77 281 (1974)
CN	XCN (X = Cl, PhSO ₂ , Ts)	Syn 784 (1977) JOMC 206 257 (1981)
CH ₂ CHR ³ OH	(LiC≡CR ⁴)/H ₂ C ^O -CHR ³ /H ⁺	TL 3461 (1976); 1363, 2465 (1978) JOC 44 1345, 3888 (1979) Tetr 36 1961 (1980) IACS 104 1774 (1982)
CH ₂ CH ₂ COR ³	H ₂ C=CHCOR ³ /H ⁺	JACS 99 253 (1977) TL 1363 (1978) JOC 44 3888 (1979) Tetr 36 1961 (1980) Pure Appl Chem 56 91 (1984)

$\text{CH}_2\text{CH}_2\text{CH}(\text{CO}_2\text{Et})_2$	$\begin{array}{c} \diagup \text{CO}_2\text{Et} \\ \diagdown \text{CO}_2\text{Et} \end{array} / \text{H}^+$	Tetr 36 1961 (1980)
$\text{C}\equiv\text{CR}^3$	$\text{XC}\equiv\text{CR}^3$ (X = Br, I, TMEDA)	TL 1465 (1975) Syn 826 (1979) Tetr 36 1215 (1980) JACS 109 7561 (1987)
	$\text{TsO}(\text{Ph})\text{IC}\equiv\text{CR}^3$	JOC 54 868 (1989)
SiMe_3	Me_3SiCl	Syn 72 (1985)
SR	RSSR	

For the formation of dienes and polyenes, see page 506, Section 3.22.

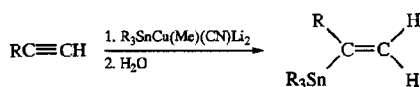


$\text{R}^1, \text{R}^2 = \text{H}, \text{H}; \text{Ph}, \text{H}; \text{R}, \text{SR}; \text{E}^+ = \text{H}_2\text{O}, \text{I}_2, \text{allylic bromide}, \text{Me}_3\text{SnCl}; \text{inter- or intramolecular}$
JACS 113 5735 (1991)

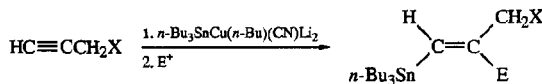


$\text{E}^+ = \text{H}^+, \text{I}_2, \text{RX}, \text{ArX} (\text{ZnBr}_2, \text{cat Pd}), \text{H}_2\text{C}=\text{CHX} (\text{ZnBr}_2, \text{cat Pd}), \text{H}_2\text{C}=\text{CHCH}_2\text{Br}, \text{R}_2\text{CO}, \text{RCOCl}, \text{CO}_2, \text{enone}, \text{epoxide}$

CC 276 (1980)
JCS Perkin I 2527 (1981)
TL 30 4913 (1989); 34 1201 (1993) (intramolecular)
JOC 54 1473 (1989); 56 770 (1991); 60 5537 (1995)
SL 981 (1992)



JOC 56 770 (1991)

XE⁺N(SiMe₃)₂H⁺, RCOCl

Syn 1201 (1991)

NHBoc

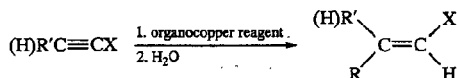
H⁺, RX, RCOCl, CO₂ /
Me₂SO₄, I₂, Me₃SiCl

Syn 1201 (1991)

SR

H⁺

SL 981 (1992)

XReagent(s)COCF₃RCu(CN)Li, R₂Cu(CN)Li₂

TL 28 5271 (1987)

COR

MeLi, CuI

JOC 51 5320 (1986)

(on HC≡CCOR)

RCu

JACS 97 1197 (1975)

R₂CuLi

JOC 41 3629 (1976); 53 1616

(1988); 55 227 (1990); 57

2766 (1992); 58 3912 (1993)

Tetr 37 4027 (1981)

TL 28 5081 (1987); 29 4913

(1988); 36 7519 (1995)

RCu(CN)Li

JOC 53 6013 (1988)

R₂Cu(CN)Li₂, (Me₃SiCl)

JOC 53 6013 (1988)

COSiPh₃R₂CuLi (R = alkyl, aryl)

SL 329 (1992)

n-Bu₃Sn(n-Bu)Cu(CN)Li₂

SL 332 (1992)

CO₂H

RCu

JACS 91 6186 (1969)

JCS C 1380 (1970)

R₂CuLi

JACS 91 6186 (1969)

CO₂R

RCu

JCS C 1380 (1970)

JACS 94 4395, 5374 (1972); 97

1197 (1975); 113 5337 (1991);

115 3146 (1993)

TL 1811 (1979); 27 5471 (1986);

28 2964 (1987)

JOC 57 2575 (1992)

JOC 56 5491 (1991)

RCu, TMEDA

RCH(OR')Cu·TMEDA·LiI,


Me₃SiClR₂CuLi

JACS 91 1851, 1853 (1969); 94

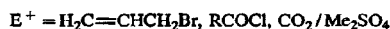
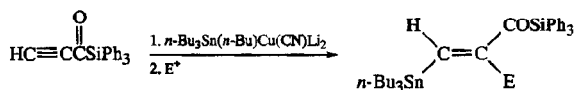
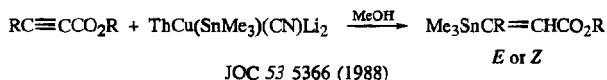
4395 (1972); 97 1197 (1975);

103 7007 (1981); 109 6199

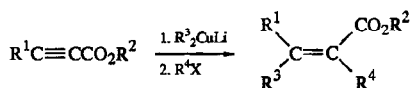
(1987); 114 2995 (1992)

		Helv 54 1939 (1971)
		Acta Chem Scand 25 1471 (1971)
		TL 1277, 1281 (1973); 1811 (1979); 21 2057 (1980); 28 2963, 5473 (1987); 30 5219 (1989); 31 3325, 3619 (1990)
		JOC 41 3629 (1976); 51 1077 (1986); 52 398 (1987); 57 2937 (1992)
		CC 1220 (1987)
		SL 660 (1994)
	$R(Me)Cu(CN)Li_2$	JACS 115 3146 (1993)
	$(ROCHR)_2Cu(CN)Li_2$	TL 29 3911 (1988)
	Me_3SiCl	JOC 55 5428 (1990); 56 5491 (1991)
	$[RCu\equiv C(CH_2)_3CH_3]Li$	JACS 94 7210 (1972)
		TL 28 2963 (1987)
	$\begin{array}{c} OSiMe_2(i-Bu) \\ \\ RC=CHCH_2Cu\equiv CSiMe_3 \end{array}Li$	JACS 107 5495 (1985)
	$\begin{array}{c} OSiMe_2(i-Bu) \\ \\ RC=C=CHCu\equiv CSiMe_3 \end{array}Li$	TL 28 1299 (1987)
	$RCu(CN)ZnX$	TL 31 1833 (1990)
		JOC 56 5974 (1991); 57 5425 (1992)
	$RCO_2CHRCu(CN)ZnBr$	JOC 55 4791 (1990); 58 588 (1993)
		JOC 58 588 (1993)
	$R_2Zn, CuCN \cdot 2LiCl$	JOC 57 1956 (1992); 60 3311 (1995)
		SL 410 (1994)
CONH ₂	$RCu(CN)ZnX$	JOC 56 5974 (1991)
CN	$RCu \cdot MgX_2, R_2CuLi$	Syn 454 (1978)
	R_2CuLi	JACS 106 462 (1984)
CO ₂ H, CO ₂ R, CHO, COR	$RCu \cdot BR_3$	JOC 44 1744 (1979)

For the use of vinylic copper reagents and $X = COSiPh_3$ or CO_2R , see page 506, Section 3.22.

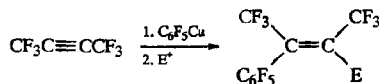


SL 332 (1992)

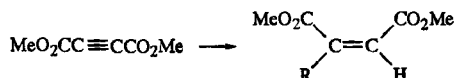


SL 660 (1994)

JOC 60 7796 (1995)

 $\text{E}^+ = \text{H}^+, \text{I}_2, \text{ArI}, \text{MeI}, \text{H}_2\text{C}=\text{CHCH}_2\text{Br}, \text{RCOCl}$

JOC 58 4411 (1993)

 $\text{MeCu}/\text{H}_2\text{O}$

JACS 95 6149 (1973)

 $\text{RCu}\cdot\text{MgX}_2/\text{H}_2\text{O}$

CL 905 (1981)

TL 36 6301 (1995)

 $\text{RCu}\cdot\text{BR}'_3/\text{H}_2\text{O}$

JOC 44 1744 (1979)

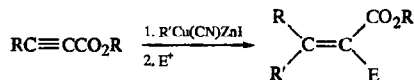
 $\text{RCu}(\text{CN})\text{ZnBr}$

JOC 55 4791 (1990); 56 5974 (1991);

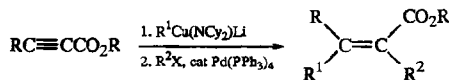
58 588 (1993)

 $\text{X} = \text{R}, \text{OR}; \text{E}^+ = \text{H}_2\text{C}=\text{CHCH}_2\text{Br}, \text{RCHO}, \text{R}_2\text{CO}$

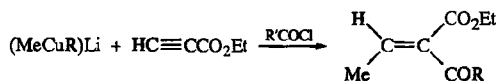
JOC 48 4621 (1983)

 $\text{E}^+ = \text{H}_2\text{O}, \text{Me}_3\text{SiCl}$

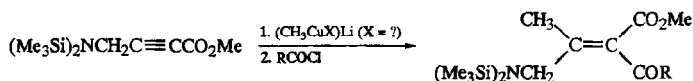
TL 30 4799 (1989)

 $\text{R}^1 = \text{Me}, n\text{-Bu}, \text{Ph}; \text{R}^2 = \text{benzylic}, \text{aryl}, \text{vinyl}$

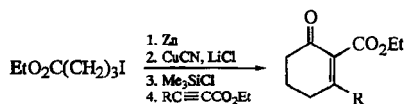
JOC 53 607 (1988)



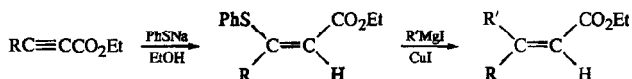
JOC 46 3696 (1981)



TL 28 2963 (1987)

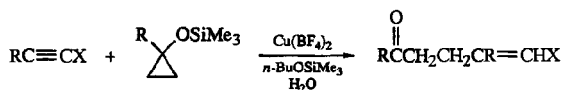


TL 36 7061 (1995)

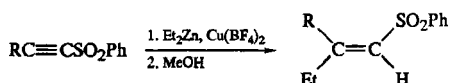


CL 705 (1974)

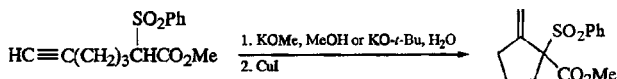
TL 28 5473 (1987)

X = COR, CO₂R, SO₂R

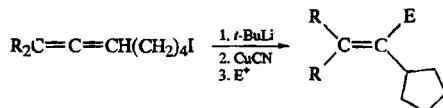
JACS 115 12330 (1993)



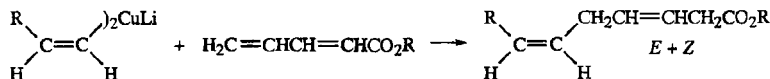
JACS 115 12330 (1993)



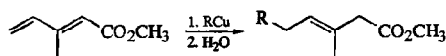
SL 227 (1992)

E⁺ = H₂O, I₂, enone (1,4-addition)

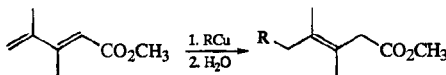
TL 33 5311 (1992)



See page 506, Section 3.22.

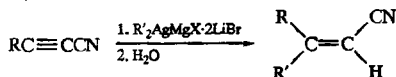


TL 1611 (1973)



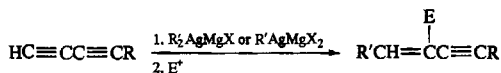
TL 1611 (1973)

2.29. Organosilver Compounds



TL 3327 (1979)

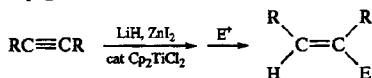
JOMC 206 257 (1981)

 $\text{E}^+ = \text{NBS}, \text{I}_2, \text{H}_2\text{C}=\text{CHCH}_2\text{Br}, \text{CO}_2$

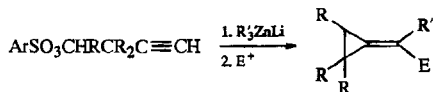
Rec Trav Chim 100 337 (1981)

2.30. Organozinc Compounds

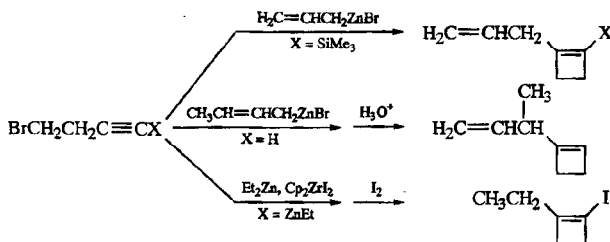
See page 438, Section 2.14, and page 452, Section 2.28.

 $\text{E}^+ = \text{D}_2\text{O}, \text{NBS}, \text{I}_2, \text{RX}$ [cat $\text{Pd}(\text{PPh}_3)_4$; $\text{R} = \text{PhCH}_2, \text{Ar}, \text{vinylic}, \text{RCO}$]

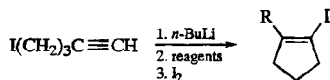
JOC 60 290 (1995)

 $\text{E}^+ = \text{H}_2\text{O}, \text{D}_2\text{O}, \text{I}_2, \text{Me}_3\text{SiCl}, \text{TsCN}$ ($\text{E} = \text{CN}$), ClCO_2Et [cat $\text{PdCl}_2(\text{PPh}_3)_2$], $\text{RCOCl}, \text{RCHO}$

JOC 60 5370 (1995)



JACS 106 6105 (1984)

RReagents

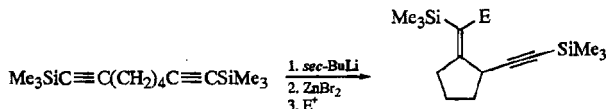
Me

Me₂AlCl / Me₃Al, cat Cp₂ZrCl₂

Et

EtZnCl / Et₂Zn, Cp₂ZrI₂CH₂CH=CH₂EtZnCl / H₂C=CHCH₂ZnBr

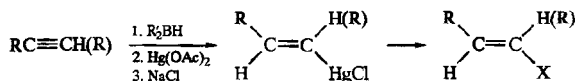
JOC 53 914 (1988)

E⁺ = H₃O⁺; I₂; CuCN, LiCl, H₂C=CHCH₂Br; RCH=CHI, Pd catalyst

TL 35 5645 (1994)

2.31. Organomercury Compounds

See also page 515, Section 3.25.

XReagent(s)CH₃CH₃RhI₂(PPh₃)₂

TL 22 2443 (1981)

JOMC 225 31 (1982)

R¹R₂CuLi (R¹ = alkyl, vinyl)

Organomet 1 74 (1982)

COR¹R¹COCl, AlCl₃

JOC 43 710 (1978)

CO₂R¹CO, R¹OH, CuCl₂, cat PdCl₂
(R¹ = H, alkyl)

JOC 40 3237 (1975)

COCH=CHR

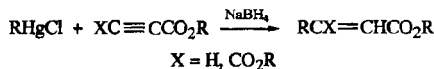
CO, cat [ClRh(CO)₂]₂

JOC 45 3840 (1980)

OAc

Hg(OAc)₂, cat Pd(OAc)₂

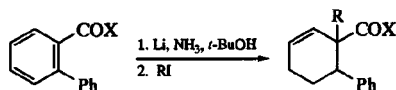
JACS 102 1966 (1980)



Angew Int 21 768 (1982); 26 479 (1987)

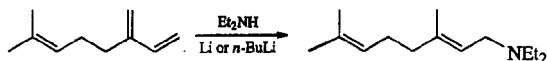
2.32. Miscellaneous Reactions

See also page 655, Section 4.



X = OR, NR₂

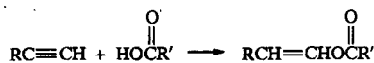
JOC 53 2456 (1988)



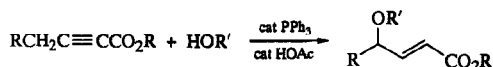
See page 761, Section 3.



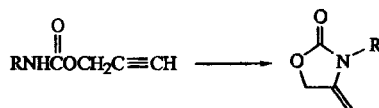
See page 1176, Section 2.2.



See page 1636, Section 5.



JACS 116 10819 (1994)



R

Ar, ArCH₂, H₂C=CHCH₂

RCO

Ts

Reagent

KO-*t*-Bu, (CuCl)

KO-*t*-Bu, AgNCO or CuCl

Et₃N, CuCl

TL 31 4887 (1990)

7. DIENES AND POLYENES

See also page 403, Section 1 for reduction of enynes and diynes to dienes.

Reviews:

A. S. Onishchenko, "Diene Synthesis," D. Davey Co., New York (1964)

Houben-Weyl, Vol V/1c, G. Thieme, Stuttgart (1970)

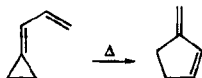
Houben-Weyl, Vol V/1d, G. Thieme, Stuttgart (1972)

Tetr 33 1845 (1977) (insect pheromones)

Syn 817 (1977) (insect pheromones)

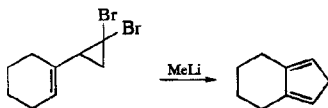
1. Rearrangement

See page 518, Section 5.



JACS 90 4749 (1968); 94 1397 (1972); 115 10754 (1993)

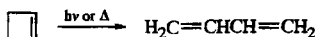
TL 3639 (1971); 1857 (1972)



Can J Chem 56 80 (1978)

JACS 106 8225 (1984)

Org Syn Coll Vol 8 223 (1993)



Angew 66 640 (1954)

Ann 675 14 (1958); 627 1 (1959)

JACS 84 4141 (1962); 87 3996 (1965); 88 1073 (1966); 90 5310, 6896 (1968); 91 5404, 7557 (1969); 93 4616 (1971); 94 4262 (1972); 101 3340 (1979); 102 3548, 6353 (1980); 103 1256 (1981); 106 7989 (1984); 107 2099, 3921 (1985); 109 6086 (1987); 112 363, 6759 (1990); 113 2163, 4019, 4993 (1991); 117 1688, 7826 (1995)

Proc Chem Soc 334 (1962)

Trans Faraday Soc 58 957 (1962)

Ber 96 2362 (1963); 97 1811, 2934 (1964)

IOC 29 257 (1964); 43 2726, 4559 (1978); 52 3708 (1987); 53 600, 2125 (1988); 54 2264, 2267 (1989); 57 1970 (1992)

TL 1207 (1965); 3387 (1974); 3047 (1975); 21 1997 (1980); 28 1501 (1987); 32 2953 (1991); 33 883 (1992); 34 1251, 1875, 6321 (1993); 35 527 (1994); 6201 (1995)

Adv Phys Org Chem 4 183 (1966)

Angew Int 7 559 (1968) (review)

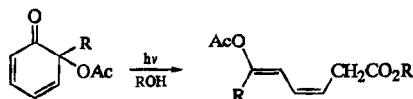
Acet Chem Res 7 65 (1974) (mechanism)

Syn Commun 12 167 (1982)

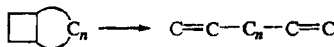
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 6.1, p 675

SL 29 (1992); 735 (1995)

Tetr 48 515 (1992)



IOC 55 5669 (1990)



hv

CC 941 (1980); 974 (1982)

TL 22 1251 (1981); 26 3579 (1985)

JACS 106 4826 (1984); 112 1998 (1990)

IOC 54 2053 (1989); 56 2170 (1991)

Δ

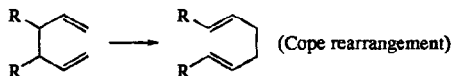
JACS 97 1510 (1975)

TCNE

JACS 103 670 (1981)

cat (Ar₃N)SbCl₆

IOC 54 2053 (1989)



(Cope rearrangement)

Org Rxs 22 1 (1975) (review)

TL 22 1583 (1981) (acid-catalyzed 2-acyl-1,5-dienes); 32 6969 (1991)

JACS 104 7225 (1982) (PdCl₂ catalyzed); 112 3945 (1990) (PdCl₂ catalyzed); 114 2635 (1992)

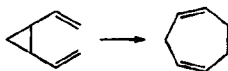
Ber 115 2309 (1982) (heteroatom substituents)

R. K. Hill in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Chpt 8 (review)

Chem Rev 84 205 (1984) (catalysis, review)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 7.1, p 785 (review)

IOC 57 1933 (1992); 60 7471 (1995)



Reviews:

Russ Chem Rev 45 469 (1976)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 8.2, p 971

Org Rxs 41 1 (1992)



Δ

Proc Chem Soc 359 (1962)

JACS 84 2775 (1962)

Tetr 21 2329 (1965)

Ber 103 426 (1970)

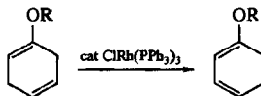
HCl

IOC 53 1713 (1988)

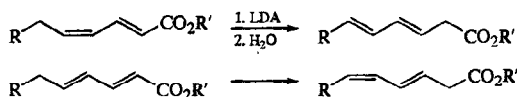
cat $C_{10}H_8 \cdot Cr(CO)_3$

JACS 110 4822 (1988); 112 4906 (1990)

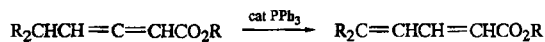
IOC 56 4569 (1991)



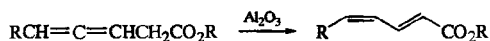
TL 3797 (1968)



CL 1541 (1984)

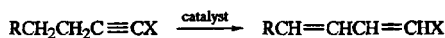


JACS 114 7933 (1992)



IOC 47 4478 (1982)

Org Syn Coll Vol 8 251 (1993)

XCatalyst

COR

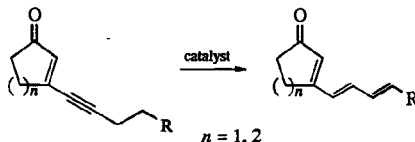
$\text{RuH}_2(\text{PPh}_3)_4$	TL 29 1045 (1988)
$\text{RuH}_2(\text{PPh}_3)_4, n\text{-Bu}_3\text{P}$	JOC 54 1105 (1989)
$\text{RuCl}_2(\text{PPh}_3)_3, n\text{-Bu}_3\text{P}$	TL 32 7549 (1991)
$\text{RuCl}_2(\text{PPh}_3)_3, \text{Ph}_3\text{P}$	JOC 54 1105 (1989)
$\text{IrH}_5(i\text{-Pr}_3\text{P})_2$	JOC 54 1105 (1989)
$\text{IrH}_5(i\text{-Pr}_3\text{P})_2, n\text{-Bu}_3\text{P}$	TL 32 7549 (1991)
$\text{Pd}(\text{OAc})_2$ or	JACS 110 2301 (1988)
$\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3, \text{PPh}_3$	TL 32 7549 (1991); 33 3659 (1992)
or dppb	

COR, CO₂R, CONR₂

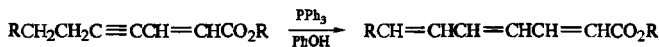
$\text{Ph}_3\text{P}, (\text{HOAc})$	JACS 114 7933 (1992)
R_3P (R = <i>n</i> -Bu, Ph)	JCS Perkin I 1921 (1993)

CO₂R

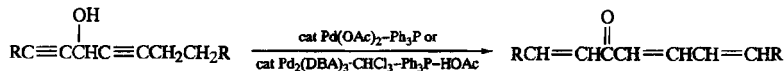
$\text{RuH}_2(\text{PPh}_3)_4, n\text{-Bu}_3\text{P}$	TL 30 843 (1989)
$\text{IrH}_5(i\text{-Pr}_3\text{P})_2, n\text{-Bu}_3\text{P}$	TL 30 843 (1989)
$\text{Pd}(\text{OAc})_2, \text{Ph}_3\text{P}$	TL 33 3659 (1992)

Catalyst: $\text{RuCl}_2(\text{PPh}_3)_3, n\text{-Bu}_3\text{P}$; $\text{RuH}_2(\text{PPh}_3)_4, n\text{-Bu}_3\text{P}$; or $\text{IrH}_5(i\text{-Pr}_3\text{P})_2$

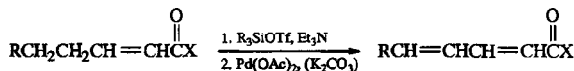
SL 357 (1990)



JOC 59 2659 (1994)

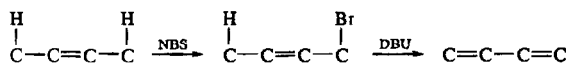


SL 405 (1992)

2. Elimination ReactionsX = R, OR, NR₂

SL 435 (1993)

JOC 59 5983 (1994)



JACS 109 2212 (1987)

XReagent(s)

Cl

AgOTf, 2,6-di-*tert*-butyl-4-methylpyridine

TL 34 6021 (1993)

Br

DBU

JACS 112 8578 (1990)

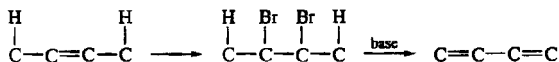
JOC 57 167 (1992)

n-Bu₄NF

JOC 60 767 (1995)



TL 36 1817 (1995)

LiCl, Li₂CO₃, HMPA

JACS 99 7899 (1977); 117 9804 (1995)

Syn 449 (1977)

JOC 55 1506 (1990)

KO-*t*-Bu

TL 28 4965 (1987)

JACS 109 2857 (1987); 110 5479, 5490 (1988)

DBN

TL 28 5833 (1987)

DBU

TL 35 7735 (1994)

KO-*t*-Bu

JOC 54 1762 (1989)

JACS 112 8889 (1990)

DBU

JOC 59 2848 (1994)

XReagent(s)

Cl

NaI

TL 30 6481 (1989)

Br

Zn

CC 508 (1966)

TL 31 423 (1990)

Zn(Hg)

Syn 742 (1982)

Zn-Cu

JOC 60 5770 (1995)

Zn-Cu, KI, I₂

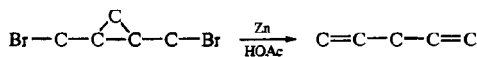
JACS 99 8 (1977); 108 512 (1986)

Zn, TiCl₄

JACS 111 3659 (1989)

cat NaBH₄-(ThTe)₂

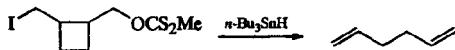
JOC 50 3170 (1985)



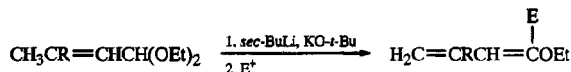
JOC 60 829 (1995)



TL 31 691 (1990)



TL 35 8513 (1994)

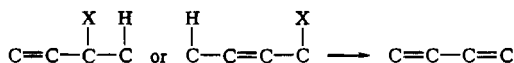
 $\text{E}^+ = \text{H}_2\text{O}, \text{D}_2\text{O}, \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCO}_2\text{R}, \text{CO}_2, \text{EtOCO}_2\text{Et}, \text{Me}_3\text{SiCl}$

JCS Perkin I 1875 (1993)

JOC 59 5458 (1994)



JOC 52 4817 (1987)

XCatalyst

OPh

 $\text{Pd}(\text{OAc})_2, \text{PPh}_3$

TL 2075 (1978)

 O_2CR $\text{Mo}(\text{NC}-t\text{-Bu})_6$

TL 33 4675 (1992)

 $\text{Pd}(\text{PPh}_3)_4; \text{HC}\equiv\text{CCH}_2\text{ZnBr}$

JOC 47 4161 (1982)

or $n\text{-Bu}_3\text{SnCH}=\text{C}=\text{CH}_2$ or

JACS 116 11151 (1994)

 $n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2$ $\text{Pd}(\text{DBA})_2, \text{PPh}_3$

TL 36 5397 (1995)

 $\text{Pd}(\text{OAc})_2, \text{PPh}_3$

TL 2075 (1978); 29 1017 (1988)

JOC 53 4886 (1988); 54 5110

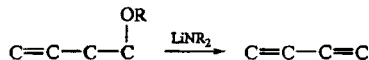
(1989)

 OCO_2Me $\text{Pd}_2(\text{DBA})_3\text{-CHCl}_3, n\text{-Bu}_3\text{P}$

TL 31 4333 (1990)

 $\text{Pd}(\text{OAc})_2, n\text{-Bu}_3\text{P}$

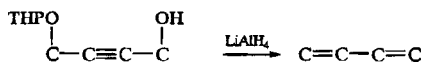
TL 33 2549 (1992)



JOC 54 777 (1989)

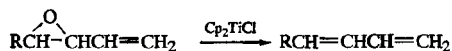


JOC 52 3560 (1987)

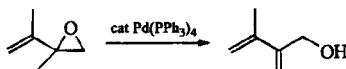


Acta Chem Scand 26 2540 (1972)

JACS 108 1338 (1986)



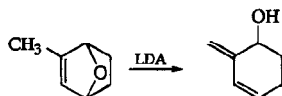
TL 33 7973 (1992)



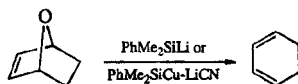
JACS 101 1623 (1979)



TL 35 3625 (1994)



TL 36 6157 (1995)



JOC 57 4065 (1992)



alumina, 500°C

JACS 110 1883 (1988)

I₂

JOC 37 68 (1972)

JACS 110 1883 (1988)

I₂, (CH₃CH₂CO)₂O

JOC 37 68 (1972)

KHSO₄

JOC 37 68 (1972)

K alum

JOC 37 68 (1972)

Et₃⁺NSO₂⁻NCO₂Et

JOC 41 3524 (1976)

JACS 110 5479 (1988)

Al₂O₃

JOC 52 3541 (1987)

Tf₂O, lutidine

JOC 52 3956 (1987)

p-TsOH JACS 111 5792 (1989)

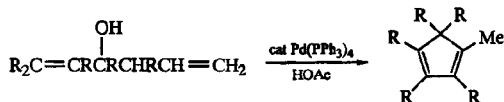
MsCl, py JOC 53 5672 (1988)

SOCl₂, py JOC 53 5672 (1988)

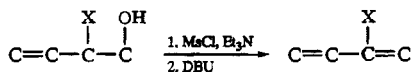
Me₃SiCl, NaI Chem Ind 956 (1982)

Et₃N⁺SO₂⁻NC(OMe)₂ JACS 111 2596 (1989)

HMPA, Δ JACS 115 11606 (1993)

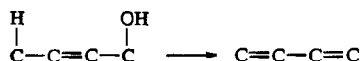


TL 32 4501 (1991)



X = CO₂Me, CN

JACS 111 643 (1989)



HF, H₂O, CH₃CN JOC 59 5983 (1994)

(C₃H₅NH)OTs TL 23 4747 (1982)

JOC 52 3541 (1987)

MsCl, py TL 31 4333 (1990)

POCl₃, py TL 33 2665 (1992)

2,4-(NO₂)₂C₆H₃SOCl, Et₃N JACS 100 5981 (1978); 104 7051 (1982); 110 3663 (1988); 112 239 (1990); 116 7658 (1994)

JOC 51 5232 (1986)

TL 29 41 (1988)

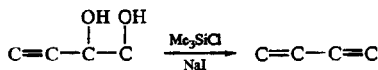
Me₃SiCl, NaI Chem Ind 956 (1982)

t-BuO₂H, VO(acac)₂/Me₃SiCl/Et₂AlTMP/ JACS 97 3252 (1975)

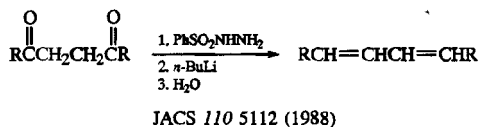
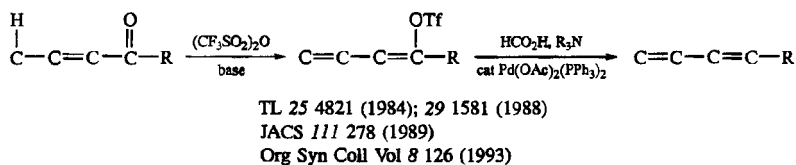
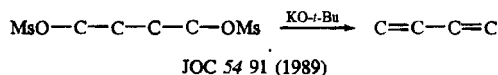
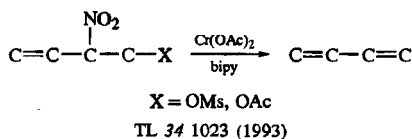
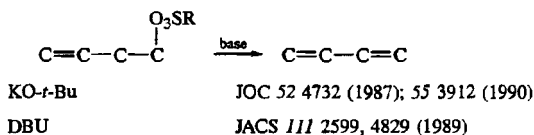
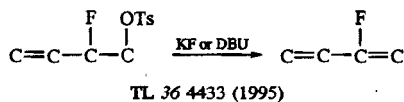
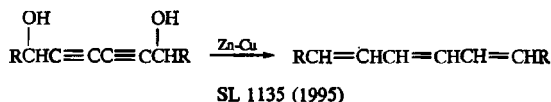
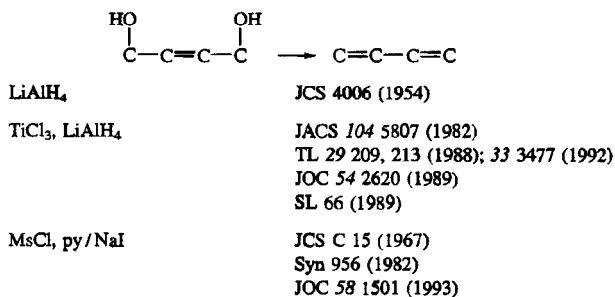
PBr₃/Zn BCSJ 52 1752 (1979)

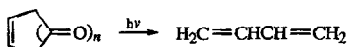


TL 33 809 (1992)

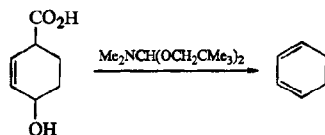


Chem Ind 956 (1982)




 $n = 1, 2$

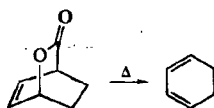
TL 35 621, 9039 (1994)



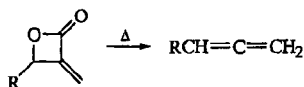
Heiv 58 1450 (1975)



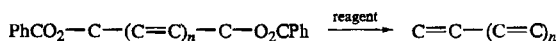
JACS 102 2841 (1980)



TL 34 7309 (1993)



JOC 58 322 (1993)

Reagent n

Na(Hg)

1, 2

TL 34 2835, 6489 (1993)

SL 548 (1993)

TiCl₃, LiAlH₄

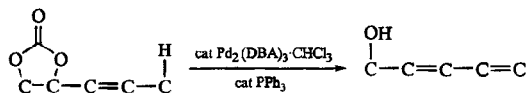
1, 2

TL 34 1803, 1807, 2835 (1993)

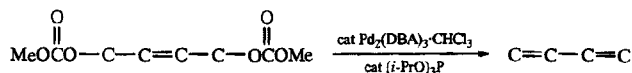
SmI₂

1, 2

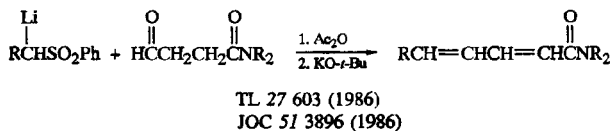
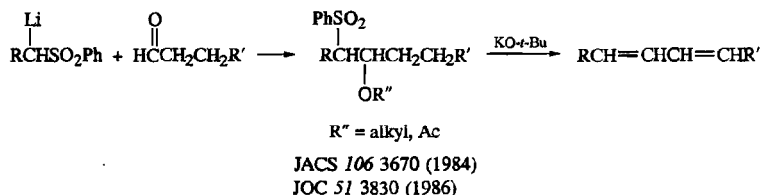
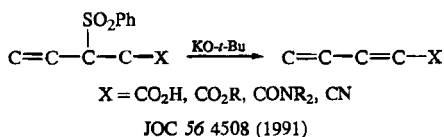
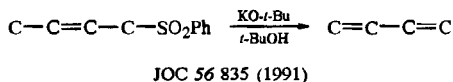
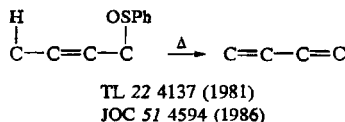
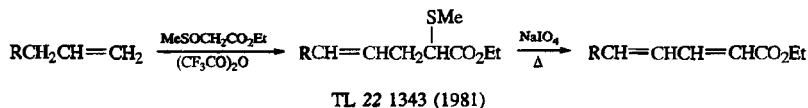
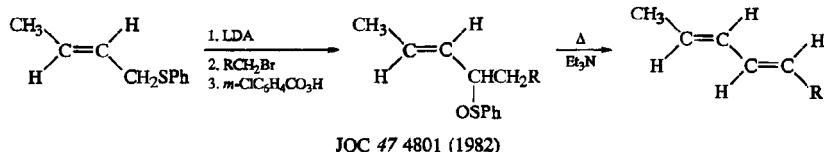
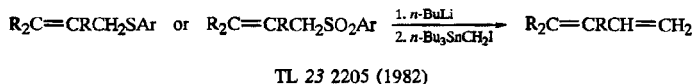
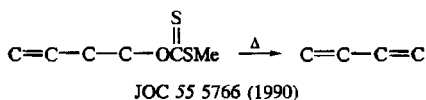
TL 34 2835 (1993)

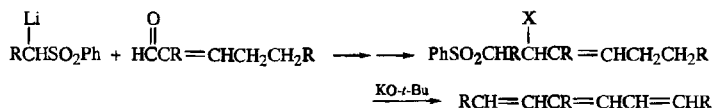


TL 36 405 (1995)



JOC 53 915 (1988)



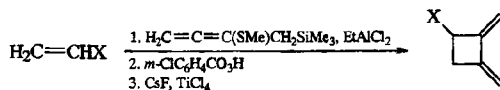


X = Cl, Br, OR

JACS 106 3670 (1984)

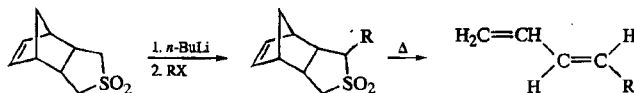
CL 1883 (1985)

JOC 51 3834 (1986)

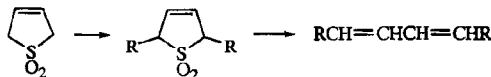


X = CO₂R, CN

TL 34 8123 (1993)



TL 23 3277 (1980)



Review: Org Prep Proc Int 21 259 (1989)

alkylation

CL 1003 (1983)

CC 1323 (1984); 236 (1985); 934 (1987)

JCS Perkin I 515 (1985); 1039 (1986)

Heterocycles 23 2913 (1985)

JOC 51 1000, 4718, 4934 (1986); 52 244, 3394,

4468, 5082 (1987); 53 69 (1988); 56 4560 (1991);

58 967 (1993)

SL 272 (1992)

elimination

h ν

JOC 39 2366 (1974)

Δ

JACS 88 2857, 2858 (1966); 97 3666 (1975)

JOC 39 2366 (1974); 52 244, 3394 (1987); 53 69,

3027, 5305 (1988); 56 4560 (1991); 58 967

(1993); 59 2010 (1994)

JCS Perkin II 1470 (1976)

CL 1003 (1983)

CC 1323 (1984); 236 (1985)

Heterocycles 23 2913 (1985)

SL 272 (1992); 397 (1993)

base, Δ

CL 1003 (1983)

JOC 51 4934 (1986)

LiAlH₄

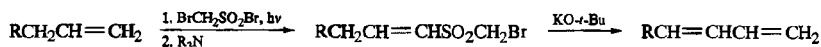
TL 947 (1977)

CL 1003 (1983)

JOC 51 4934 (1986); 52 4468, 5082 (1987); 56 4560 (1991)

K, ultrasound

JOC 52 2224 (1987)



JACS 105 6164, 6165 (1983); 108 4568 (1986)

TL 25 5469 (1984)

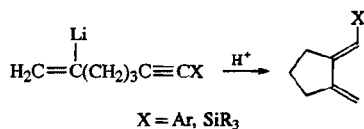
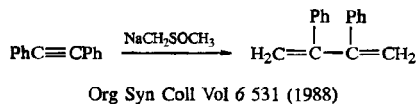
Org Syn 65 90 (1987)

3. Organometallic Approaches

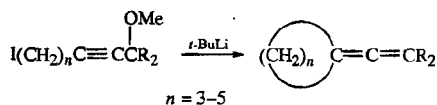
For symmetrical coupling of allylic and vinylic halides or alcohols, see also page 77, Section 1.

3.1. Organolithium and -sodium Compounds

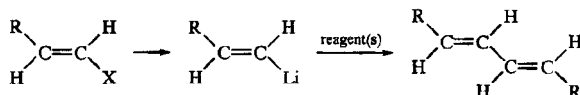
See also page 506, Section 3.22.



JOC 59 5868 (1994)



JOC 60 754 (1995)



Reagent(s)

CoCl₂

JOMC 24 537 (1970)

JACS 110 1883 (1988)

Reagent(s) $(n\text{-Bu}_3\text{P}\cdot\text{CuI})_4 / \text{O}_2$

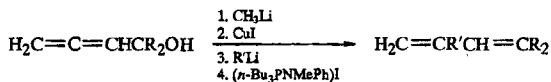
JACS 89 5302 (1967)

 CuI or $(n\text{-Bu}_3\text{P}\cdot\text{CuI})_4$ or $(n\text{-Bu}_3\text{P}\cdot\text{AgI})_4$

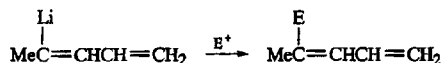
JACS 93 1379 (1971)

 AgI

JOC 36 1694 (1971)



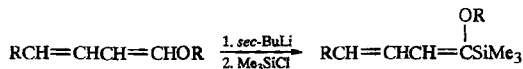
TL 29 1701 (1988)

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}$

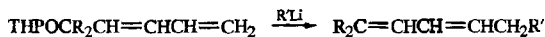
JOC 45 4263 (1980)



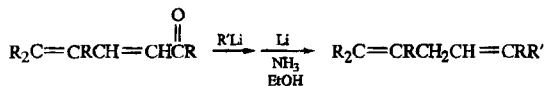
JOC 51 4492 (1986)



JOC 52 4818 (1987)

 $\text{R}' = 1^\circ, 2^\circ \text{ alkyl; NEt}_2; \text{SiMe}_2\text{Ph; SnMe}_3$

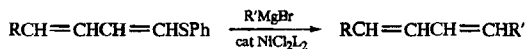
JOC 52 4416 (1987)



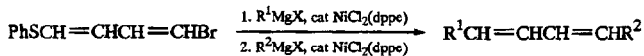
JOC 44 1159 (1979)

3.2. Organomagnesium Compounds

See also page 420, Section 2.6; page 506, Section 3.22; and page 514, Section 3.24.



TL 29 3705 (1988)



TL 35 8847 (1994)



TL 36 3901 (1995)

CatalystCuI or Pd(PPh₃)₄R

1° alkyl, 1° benzylic, aryl

BCSJ 2831 (1981)

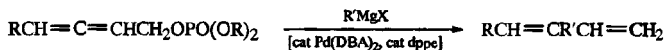
Li₂CuCl₄

1° alkyl

TL 24 1003 (1983)

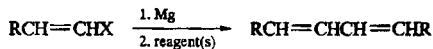
JOC 53 318 (1988)

JACS 114 3044 (1992)



TL 25 203 (1984)

Tetr 40 3645 (1984); 41 867 (1985)

Reagent(s)SOCl₂

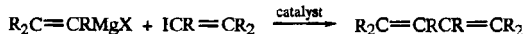
JOC 37 3749 (1972)

RN=OCl₂, cat Pd(PPh₃)₄

TL 29 5379 (1988)

CuCl

Angew Int 6 85 (1967)

Catalyst

Ni

BCSJ 49 1958 (1976)

TL 29 3705 (1988)

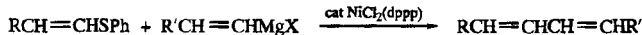
Pd

JOMC 91 C39 (1975)

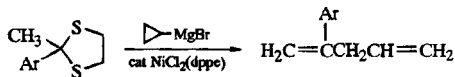
TL 191 (1978); 29 3705 (1988)

JOC 44 2408 (1979); 59 5527 (1994)

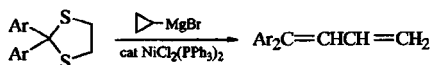
SL 665 (1994)



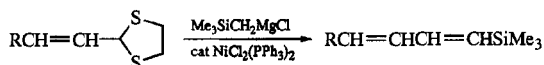
JOC 58 5351 (1993)



JOC 56 4035 (1991)

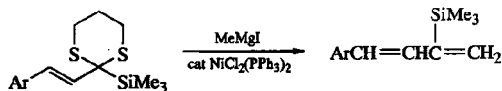


JACS 111 9119 (1989); 112 9356 (1990)

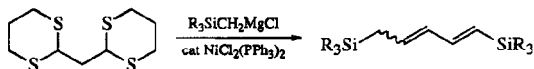


JOC 53 5582 (1988)

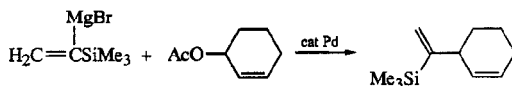
JACS 112 9356 (1990)



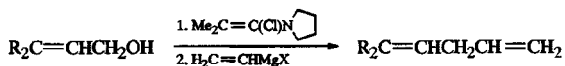
JACS 112 9356 (1990)



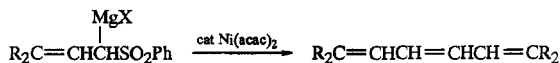
JACS 114 7308 (1992)



TL 31 77 (1990)



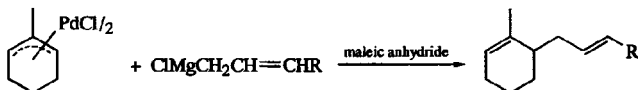
TL 24 5745 (1983)



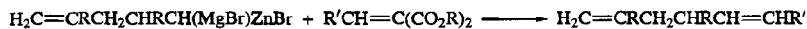
TL 23 2457 (1982)



JACS 115 5879 (1993)

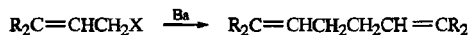


JACS 106 5029 (1984)

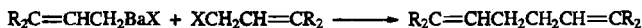


JOC 55 5446 (1990)

3.3. Organobarium Compounds



JOC 57 6386 (1992)



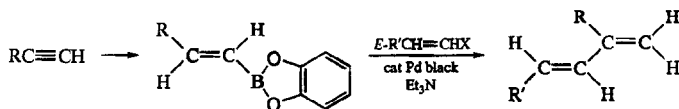
JOC 57 6386 (1992)

TL 33 6435 (1992); 34 5995 (1993); 36 6301 (1995)

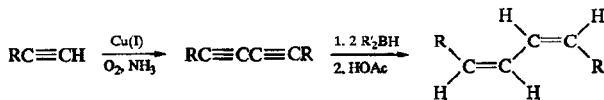
JACS 117 670 (1995)

3.4. Organoboron Compounds

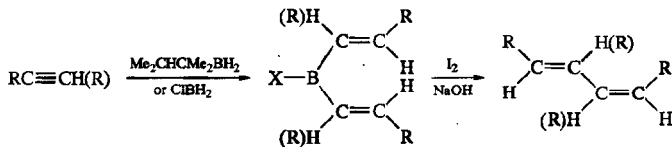
See also page 421, Section 2.8.



JOMC 213 C53 (1981)

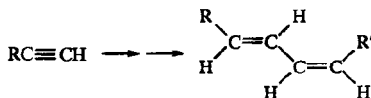


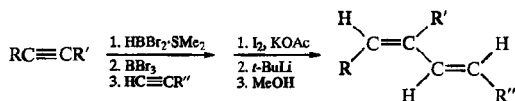
JACS 92 4068 (1970)



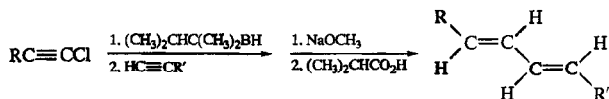
JACS 90 6243 (1968)

JOC 38 1617 (1973)

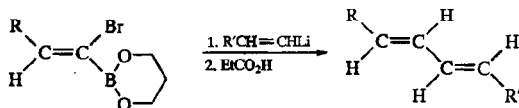
(Sia)₂BH/R'C≡CLi/I₂, NaOH/(Sia)₂BH/HOAc CC 874 (1973)Cy₂BH/R'C≡CLi/BF₃·OEt₂ or *n*-Bu₃SnCl/HOAc JOMC 156 159 (1978)



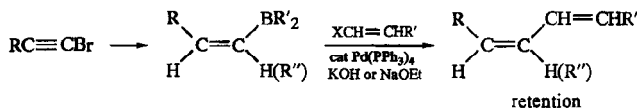
TL 27 977 (1986)



CC 606 (1973)

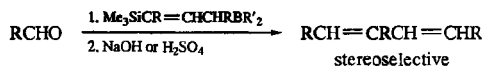


TL 32 3655 (1991)



TL 27 3745 (1986)

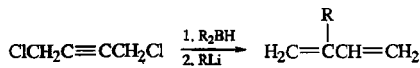
CL 1329 (1986)



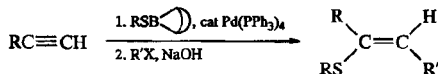
TL 22 275 (1981); 33 5025 (1992)

JOC 54 5814 (1989); 55 5719 (1990); 56 1914 (1991); 57 796 (1992)

JACS 112 4424 (1990)

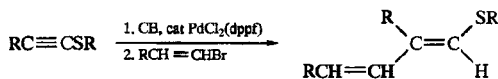


CC 531, 1629 (1987)

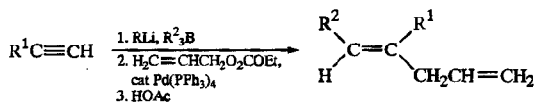


R' = vinylic, allylic

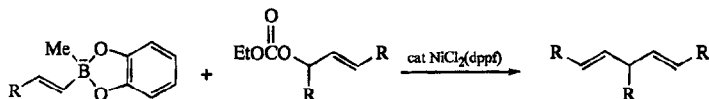
JACS 115 7219 (1993)



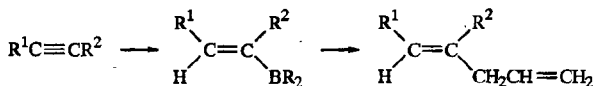
JOC 58 5351 (1993)



TL 31 2405 (1990)



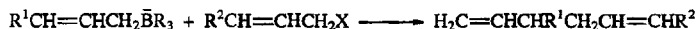
SL 571 (1995)



See page 421, Section 2.8.



Syn Commun 12 813 (1982)

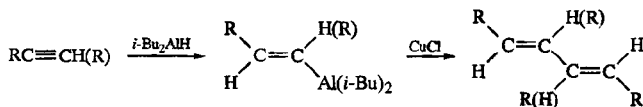


X = Cl, Br

JACS 100 6282 (1978); 103 1969 (1981)

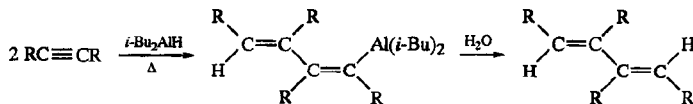
3.5. Organoaluminum Compounds

See also page 427, Section 2.9, and page 506, Section 3.22.

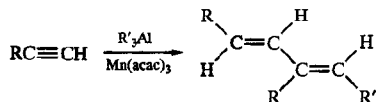


JACS 92 6678 (1970)

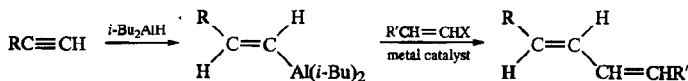
JOC 55 826 (1990)



Ann 629 222 (1960)



JOC 44 1496 (1979)

X

Cl, Br, I

Metal

Ni

Pd

JACS 109 2393 (1987)

JACS 98 6729 (1976); 109 2393 (1987)

TL 28 1649, 4875 (1987); 29 2239 (1988); 32 4453 (1991)

JOC 55 826 (1990)

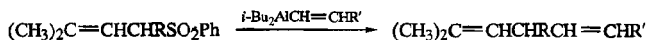
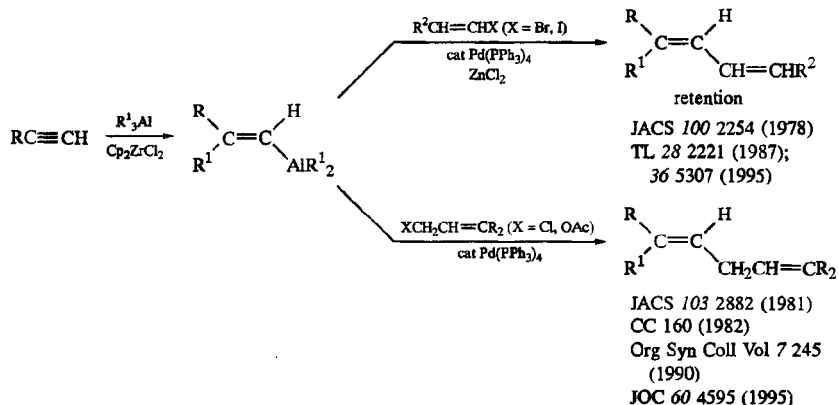
Org Syn Coll Vol 8 295 (1993)

OPO(OPh)₂

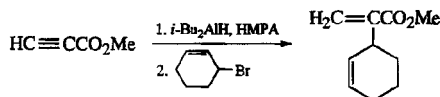
Pd

TL 21 2531 (1980); 22 1609 (1981)

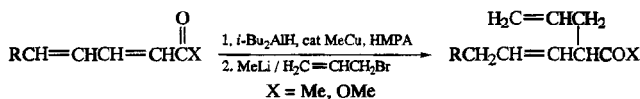
BCSJ 57 108 (1984)



JACS 108 1098 (1986)

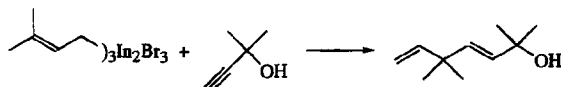


JOC 52 1624 (1987)



JOC 52 439 (1987)

3.6. Organoindium Compounds



TL 33 2581 (1992)

JOC 60 1841 (1995)

3.7. Organosilicon Compounds

See also page 487, Section 3.8, and page 494, Section 3.13.

 E^+ $\text{RCH}(\text{OR}')_2, \text{BF}_3 \cdot \text{OEt}_2$

TL 21 3783 (1980)

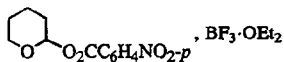
 $\text{RCH}(\text{OR}')_2, \text{TiCl}_4$

TL 21 3783 (1980)

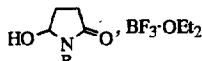
Organomet 1 1651 (1982)

 $\text{R}_2\text{C}(\text{OR}')_2, \text{TiCl}_4$

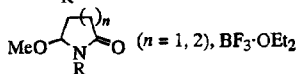
Organomet 1 1651 (1982)



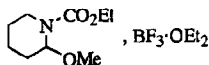
TL 25 5743 (1984)



JOC 59 6480 (1994)



JOC 59 6480 (1994)



JOC 59 6480 (1994)

 $\text{RCHO}, \text{BF}_3 \cdot \text{OEt}_2$

TL 21 3783 (1980)

Tetr 48 2385 (1992)

 $\text{RCHO}, \text{TiCl}_4$

JOC 45 1721 (1980)

Organomet 1 1651 (1982)

JACS 106 3240 (1984)

TL 28 5921 (1987)

 $\text{R}_2\text{CO}, \text{TiCl}_4$

JOC 45 1721 (1980)

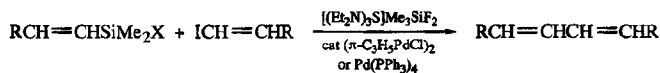
Organomet 1 1651 (1982)

 $\text{RCOCl}, \text{AlCl}_3$

CL 2037 (1987)

 $\text{RCOCl}, \text{TiCl}_4$

TL 21 3783 (1980)

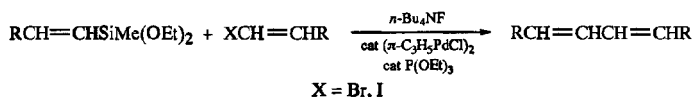
 X

F

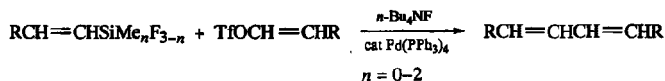
JOC 54 268 (1989)

Me

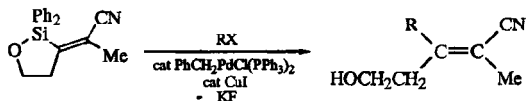
JOC 53 918 (1988)



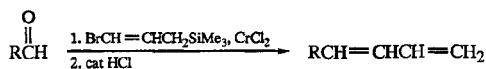
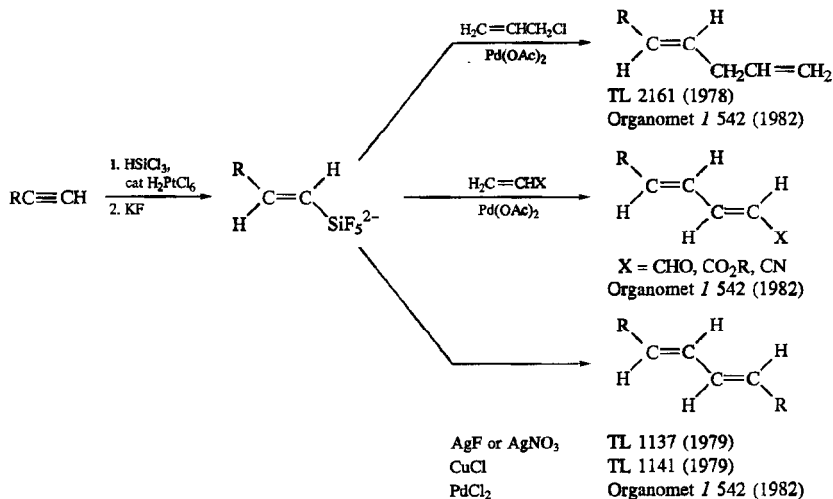
TL 30 6051 (1989)



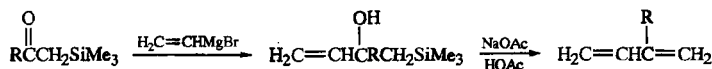
TL 31 2719 (1990)



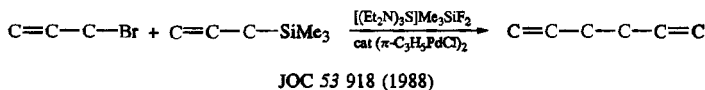
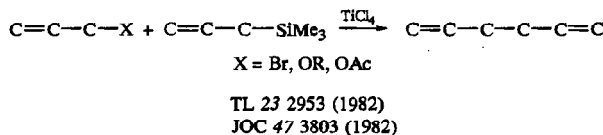
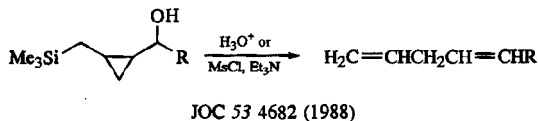
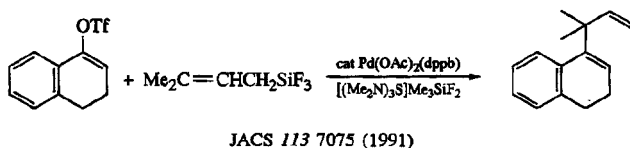
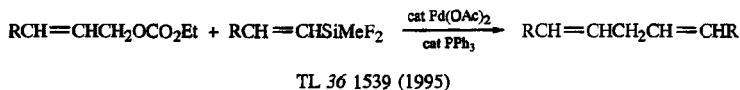
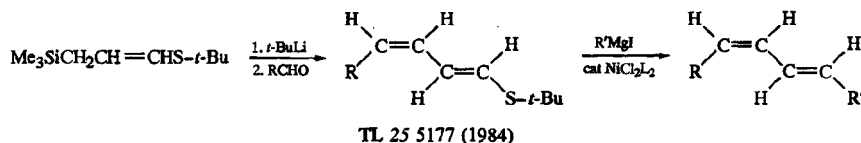
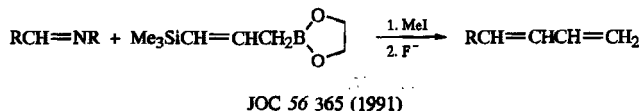
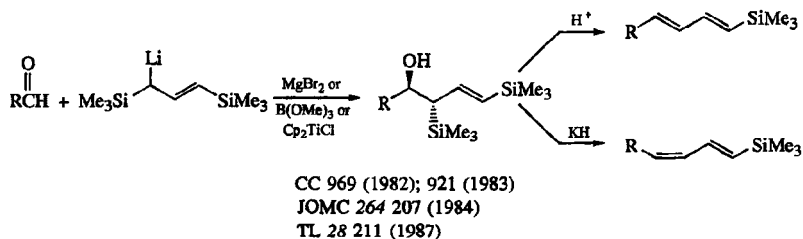
TL 35 8635 (1994)

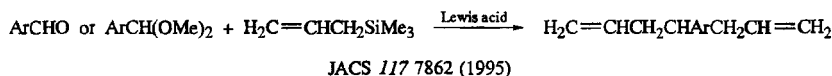
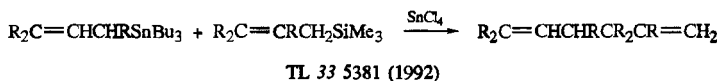
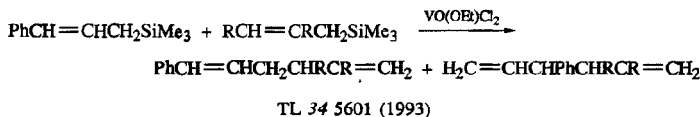
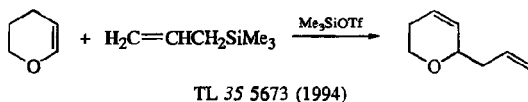
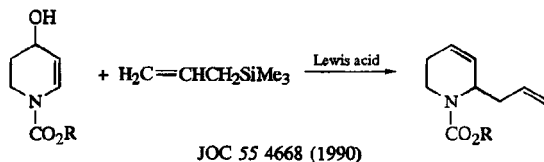
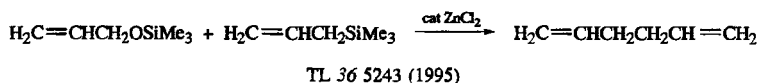
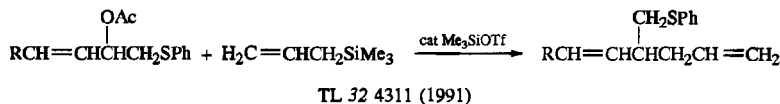
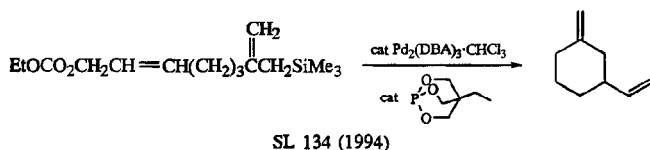
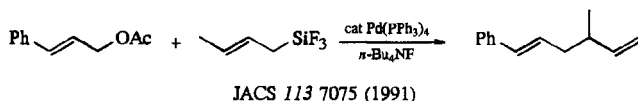


SL 599 (1992)



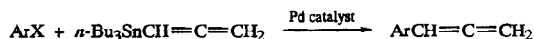
TL 28 693, 697 (1987)





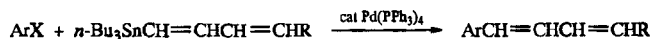
3.8. Organotin Compounds

See also page 434, Section 2.11; page 484, Section 3.7; page 494, Section 3.13; and page 501, Section 3.21.

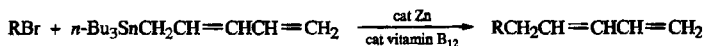


Syn Commun 24 789 (1994) (X = I)

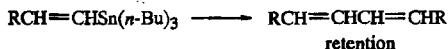
TL 35 5477 (1994) (X = OTf)



SL 817 (1995)



SL 237 (1994)



cat $\text{PdCl}_2(\text{PPh}_3)_2$, O_2

JACS 117 10905 (1995) (intramolecular)

cat $\text{PdCl}_2(\text{PPh}_3)_2$, cat CuI , air

JACS 115 9048 (1993)

$n\text{-BuLi}$ / CuCl_2 , cat $\text{PdCl}_2(\text{CH}_3\text{CN})_2$

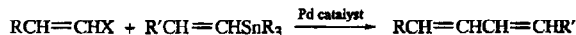
TL 34 5649 (1993)

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$

JOC 52 4296 (1987)

TL 33 4649 (1992); 36 283 (1995)

JACS 117 10905 (1995)



X

Cl, Br, I

JACS 108 1359 (1986); 109 813 (1987); 112 3497, 4070 (1990); 113 9693 (1991) (triene); 114 2260, 9434 (1992); 115 4419, 4497, 5815, 9048, 9327, 9842 (1993); 117 5407 (intramolecular), 8258 (1995)

JOC 53 926 (1988) (intramolecular); 55 3114, 4995, 5359 (1990); 56 4821 (1991); 57 1958 (1992); 58 1443, 3953, 7870 (1993); 59 332, 2695, 4143, 5662 (1994)

TL 30 2911, 3645, 4299 (1989); 31 307, 4293, 6077 (1990); 32 3391, 4397, 4453 (1991); 33 409, 919, 7589 (1992); 34 2429, 4485, 6559 (1993); 35 1027, 2081, 4911, 5177, 6551 (1994); 36 2469, 3389, 3605, 3687, 4741 (1995)

SL 53, 157, 614, 741 (1991); 332 (1992); 215 (intramolecular), 573, 693 (1993); 524, 998 (1994); 267 (intramolecular), 903, 1247, 1264 (1995)

⁺
IPh

TL 33 4095 (1992)

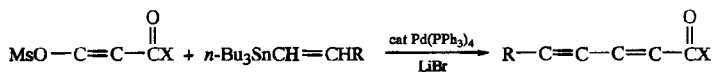
JACS 115 11626 (1993)

OSO_2F

TL 32 4073 (1991)

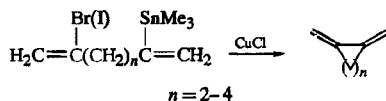
OTf

JACS 106 4630 (1984); 108 3033 (1986); 109 3785 (1987) (intramolecular, macrocyclic lactones); 111 1522, 5417 (1989); 112 8997 (1990); 113 9585 (1991); 114 7692, 8333 (1992); 115 1619 (1993); 116 11323 (1994)
 CC 809 (1985) (intramolecular)
 TL 27 5595 (1986); 29 1417, 6043 (1988); 31 1347, 1889 (1990); 32 6675 (1991); 34 1433 (1993); 35 2509 (1994); 36 4051, 4303 (1995)
 JOC 54 1483 (intramolecular), 3334, 5828 (1989); 55 2443, 3114, 4995, 5008, 5359, 5613, 5833 (1990); 56 4317 (1991); 57 4043, 5301 (1992); 60 6608, 7821 (1995)
 SL 351 (1992); 365 (1993); 152, 967 (1994)
 Org Syn Coll Vol 8 97 (1993)

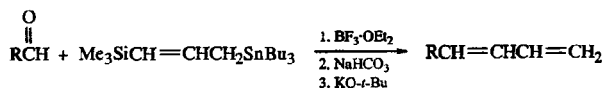


X = R, OR

JOC 56 1489 (1991)



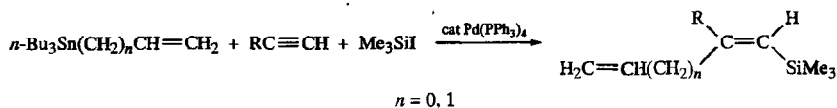
JOC 58 3609 (1993)



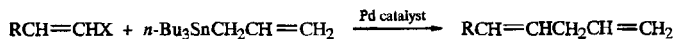
JOMC 292 311 (1985)

JOC 58 6083 (1993)

See also page 494, Section 3.13.



JACS 113 7778 (1991)

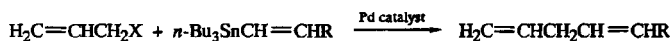


$$\begin{matrix} \text{X} \\ | \\ \text{I}^+\text{Ph} \end{matrix}$$

TL 33 4095 (1992)

OTf

JACS 106 4630 (1984)
 JOC 55 5833 (1990)
 TL 32 157, 6675 (1991)



X

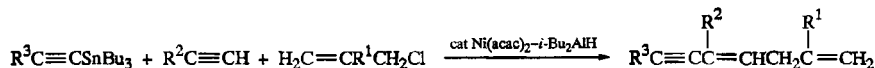
Cl, Br

JACS 105 7173 (1983); 106 4833 (1984); 112 2813 (1990); 113 9585 (1991); 115 1619 (1993)
TL 29 1417, 5739 (1988); 33 773, 777 (1992); 35 4577 (1994)

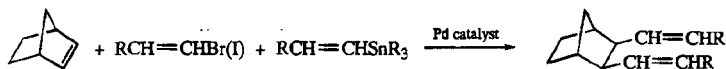
JOC 55 5833 (1990); 59 2695, 4143, 7917 (1994)
SL 152, 181 (intramolecular) (1994)

OAc

JOC 55 3019 (1990)

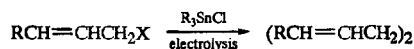


JOC 59 6877 (1994)



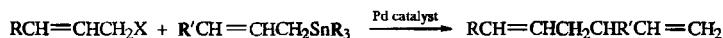
Tetr 45 961 (1989)

BCSJ 66 3522 (1993)



X = halogen, OAc

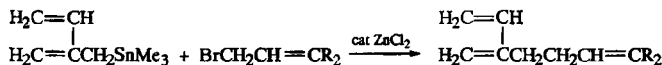
TL 27 4469 (1986)



X = Cl, Br, OAc

TL 21 2595, 2599 (1980); 29 5739 (1988)

JOC 55 3118 (1990)

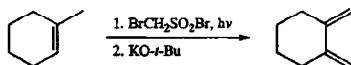


TL 24 1905 (1983)



TL 34 4497 (1993)

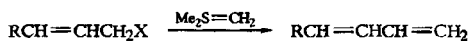
3.9. Sulfur Reagents



JACS 105 6164, 6165 (1983)

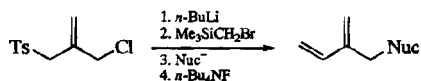
TL 25 5469 (1984)

Org Syn Coll Vol 8 212 (1993)



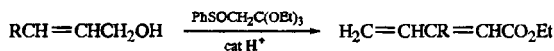
X = Cl, Br, OMs

TL 35 5453 (1994)

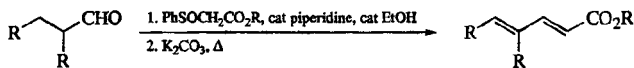


Nuc⁻ = R₂NH, NaN₃, NaSPh, RCO₂H (NaI, CsF), RMgX

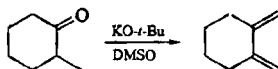
TL 34 3781 (1993)



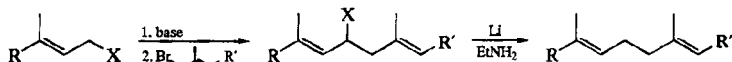
JOC 56 6981 (1991); 60 4617 (1995)



CL 781 (1980)



SL 23 (1991)



X

SPh

TL 3707 (1969); 27 2157 (1986)

Tetr 27 5861 (1971)

Proc Natl Acad Sci USA 68 1294 (1971)

JACS 95 4444 (1973)

Syn 129 (1974)

JOC 45 4097 (1980)

SO₂Ph

BSCF 746 (1973)

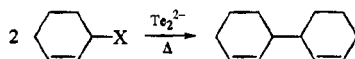
JOC 39 2135 (1974); 57 2794 (1992)

JCS Perkin I 761 (1981)

CL 25 (1981) (intramolecular); 725 (1983)

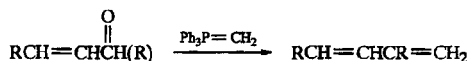
CC 1761 (1986); 1036 (1987)

3.10. Tellurium Reagents

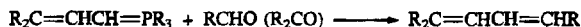


JOC 47 1641 (1982)

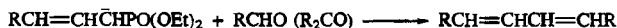
3.11. Phosphorus Reagents



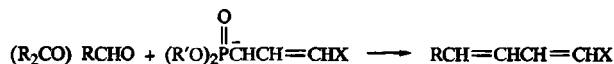
JOC 56 989 (1991)

JOC 49 210 (1984); 52 4121 (1987); 53 2723, 2937 (1988); 54 915, 4088 (1989)
SL 123 (1991)

JOC 53 4124 (1988); 57 5208 (1992)

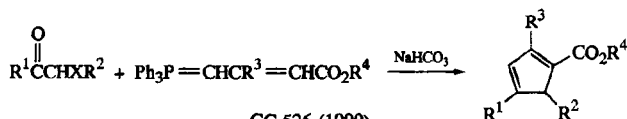
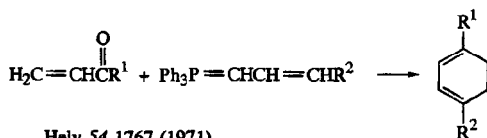
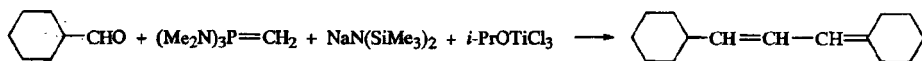


JOC 54 3359 (1989)

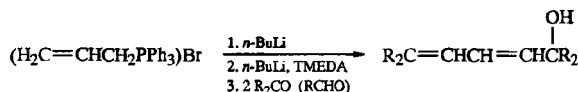
XCO₂RJOC 52 5067 (1987); 56 1192 (1991); 60 1195, 1806, 5785 (1995)
TL 28 2771 (1987)
Syn 254 (1987)
SL 1221 (1995)

CN

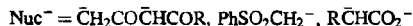
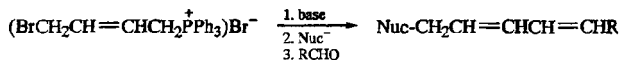
TL 27 6177 (1986); 28 259 (1987)

CC 526 (1990)
JOC 59 111 (1994)Helv 54 1767 (1971)
Ber 106 3779 (1973)
JACS 95 5088 (1973)
TL 4425 (1973)
JOC 39 1318 (1974); 42 1664 (1977); 60 1195 (1995)
CC 1705 (1984)

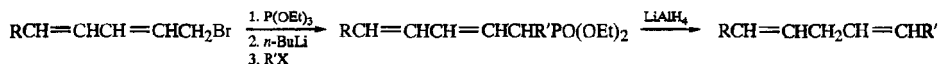
JOC 58 1298 (1993)



TL 32 4353 (1991)

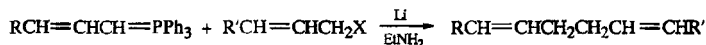


TL 33 577 (1992)



TL 245 (1979)

Ann 536 (1982)



JACS 92 2139 (1970)

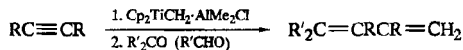


X	n	
PO(OEt)_2	1	JCS Perkin I 151 (1989) TL 34 7399 (1993)
	2	JCS Perkin I 151 (1989)
$n\text{-Bu}_3\text{P}^+$	1, 2	JCS Perkin I 151 (1989)

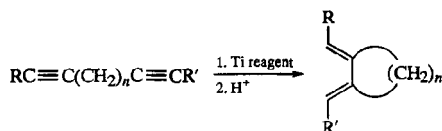


TL 1359 (1975)

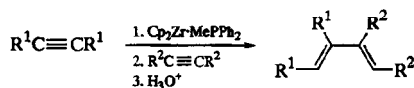
3.12. Organotitanium Compounds



TL 32 1687 (1991)



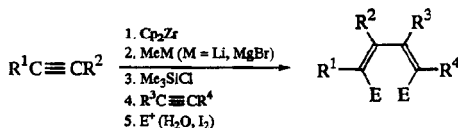
Ti reagent	n	
Cp_2TiCl_2 , Na(Hg), Ph_2PMe	3–5	JACS 106 6422 (1984); 109 2788 (1987)
$\text{Ti(O-}i\text{-Pr)}_4$, $i\text{-PrMgCl}$	3	TL 36 4261 (1995)



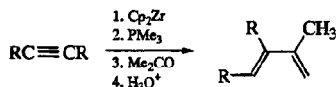
CL 623 (1987)

JACS 111 3336 (1989)

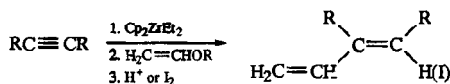
TL 30 3495 (1989)



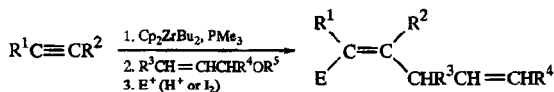
JACS 111 2870 (1989)



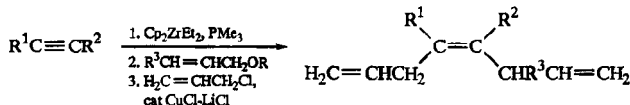
JACS 111 3336 (1989)



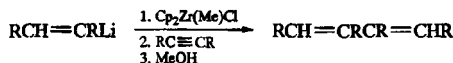
JACS 117 5871 (1995)



TL 34 4811 (1993)



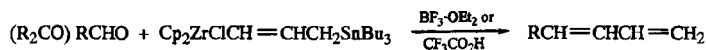
TL 35 5685 (1994)



SL 705 (1993)



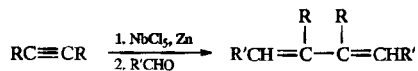
TL 33 5969 (1992)



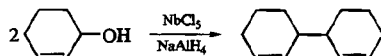
SL 341 (1993)

See also page 487, Section 3.8.

3.14. Organoniobium Compounds

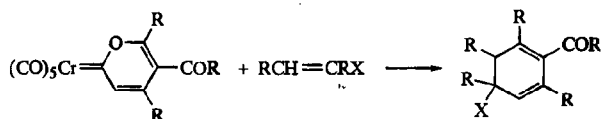


JOC 57 1973 (1992)

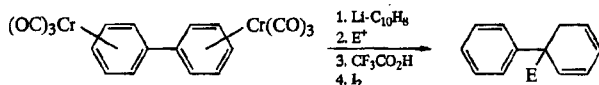


CL 157 (1982)

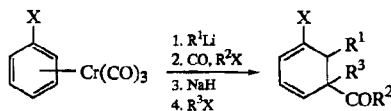
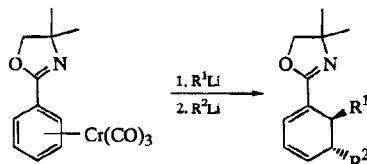
3.15. Organochromium Compounds

X = OR, NR₂

JACS 112 4550 (1990)

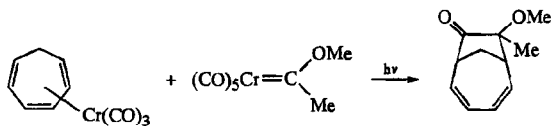
E⁺ = H⁺, RX (X = Br, I, OTs)

JACS 112 8388 (1990)

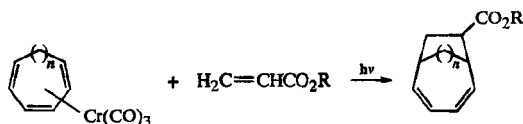


X = oxazoline or CH=NCy

JOC 59 4773 (1994)



TL 35 8131 (1994)

 $\frac{n}{n}$

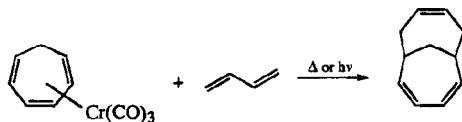
1

JACS 113 5122 (1991); 117 8851 (1995)

JOC 57 5290 (1992); 60 7392 (1995)

2

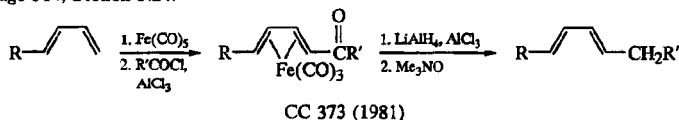
TL 36 8569 (1995)



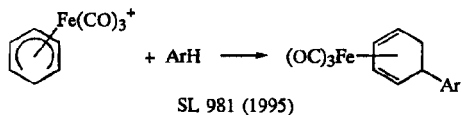
JACS 115 1382 (1993); 117 8851 (1995)

3.16. Organoliron Compounds

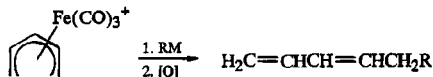
See also page 514, Section 3.24.



CC 373 (1981)



SL 981 (1995)



Review: SL 10 (1990)

RM

 $\text{Ph}_2\text{C}=\text{N}^-\text{CHCO}_2\text{Me}$

SL 631 (1994)

 $\text{CH}^-(\text{CO}_2\text{R})_2$

TL 30 2607 (1989)

SL 983 (1992)

 $\text{LiC}\equiv\text{CR}$

SL 766 (1992)

 $\text{LiC}\equiv\text{CR}, \text{CuBr}\cdot\text{SMe}_2$

SL 895 (1991)

 $\text{Me}_3\text{SiC}\equiv\text{CR}$

TL 30 1339 (1989)

 $\text{LiCu}(\text{CH}_2\text{CO}_2\text{R})_2$

SL 669 (1995)

 LiCuR_2

Austral J Chem 29 1101 (1976)

SL 983 (1992)

RM (continued)

Li(RCuSPh)

Austral J Chem 30 345 (1977)

LiCuAr₂

TL 30 2607 (1989)

SL 507 (1992)

(RC≡C)₂Cu(CN)Li₂

SL 766 (1992)

Li₂Cu(C≡CR)₃

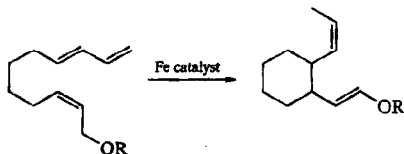
TL 30 1339 (1989)

RCu(CN)ZnI

SL 905 (1992)

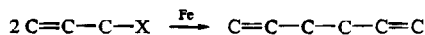
Ar₂Zn

TL 30 2607 (1989)



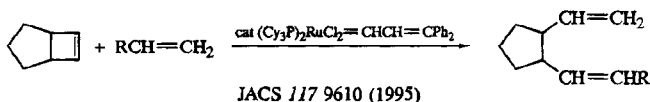
TL 31 2865 (1990); 33 317 (1992); 36 2941 (1995)

JOC 59 6928 (1994); 60 3473 (1995)

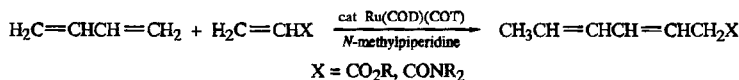


Can J Chem 47 1238 (1969)

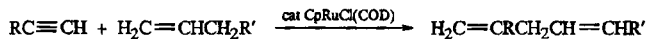
JOC 52 5560 (1987)

3.17. Organoruthenium Compounds

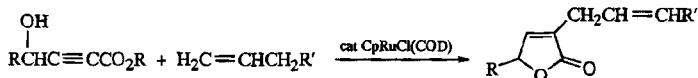
JACS 117 9610 (1995)



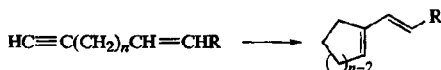
TL 33 341 (1992)



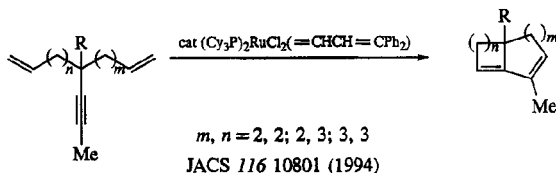
JACS 115 4361 (1993); 117 615, 1888 (1995)



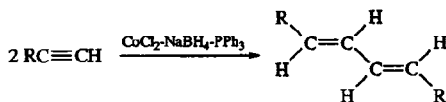
JACS 116 7459 (1994); 117 1888 (1995)



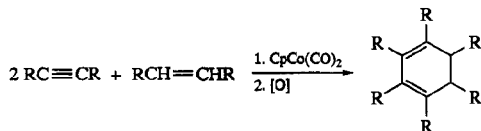
<u><i>n</i></u>	<u>Reagents</u>	
3-5	cat (Cy ₃ P) ₂ RuCl ₂ (=CHCH=CPh ₂)	SL 1020 (1994)
3, 4	CO, cat [RuCl ₂ (CO) ₃] ₂	JACS 116 6049 (1994)



3.18. Organocobalt Compounds



TL 27 6253 (1986)



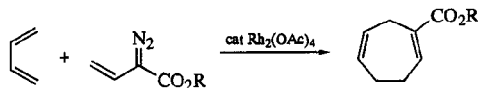
JACS 102 4839 (1980); 107 1664 (1985); 113 381 (1991) (all intramolecular)
CC 53 (1981); 388 (1986) (intramolecular)
Angew Int 20 802 (1981) (intramolecular); 23 539 (1984) (review)
JOC 47 3447 (1982) (intramolecular)

3.19. Organorhodium Compounds

See also page 515, Section 3.25.



JOMC 219 C16 (1981)



JOC 56 3817 (1991)

3.20. Organonickel Compounds

See also page 476, Section 3.2; page 479, Section 3.4; page 482, Section 3.5; page 484, Section 3.7; page 514, Section 3.24; and page 518, Section 5.



X = halogen

Ni(COD)₂, DMF

IACS 94 9234 (1973); 103 6460 (1981)

Ni(OAc)₂, NaH, *t*-AmONa, bipy

JOMC 264 263 (1984)

TL 27 3517 (1986)

cat NiCl₂(bipy), cat PbBr₂, Al

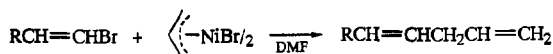
TL 30 1261 (1989)

cat NiCl₂(PEt₃)₂, Zn, KI

BCSJ 57 1887 (1984)

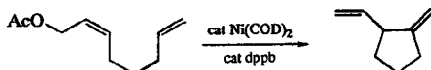


JOMC 219 C16 (1981)



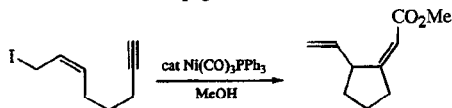
JACS 89 2755 (1967)

Org Rxs 19 115 (1972) (review)

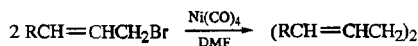


TL 29 6433 (1988); 31 1265 (1990)

See also page 501, Section 3.21.



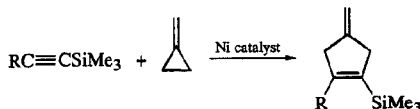
TL 29 6433 (1988)



Org Rxs 19 115 (1972) (review)

TL 28 2795 (1987)

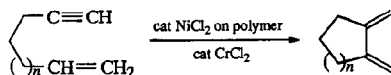
JACS 112 228, 1258 (1990); 113 4006 (1991) (all intramolecular)



Angew Int 24 316 (1985)

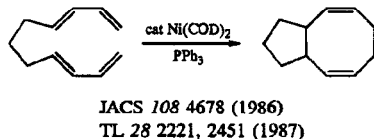
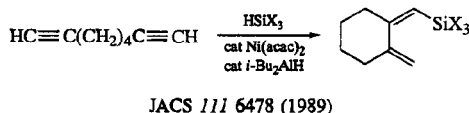
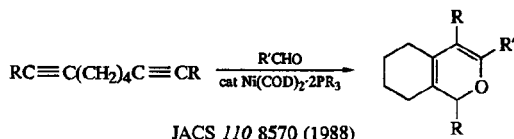
Topics Curr Chem 135 77 (1987) (review)

TL 30 7107 (1989) (intramolecular)



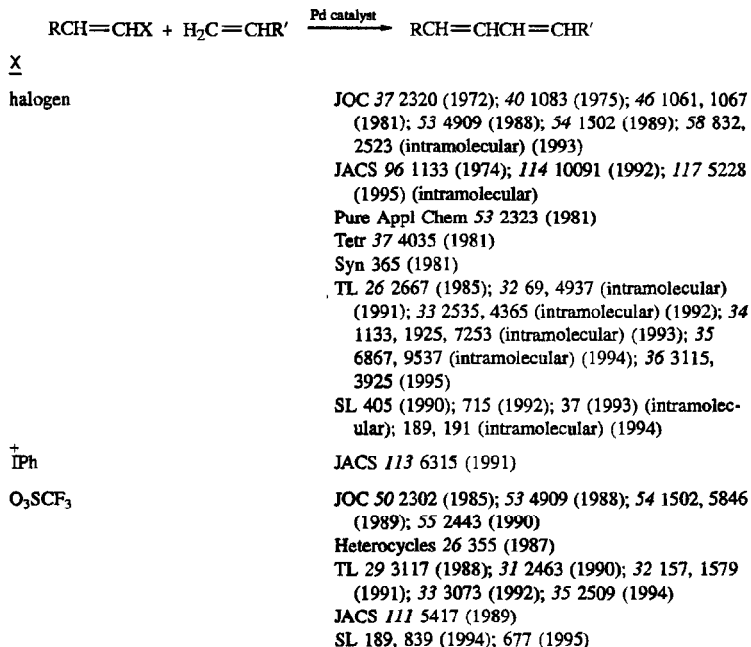
n = 1, 2

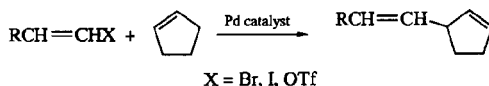
JACS 109 5268 (1987)



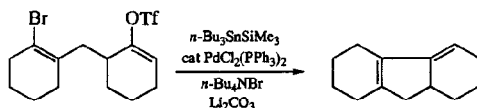
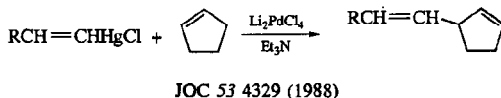
3.21. Organopalladium Compounds

See also page 448, Section 2.26; page 476, Section 3.2; page 479, Section 3.4; page 482, Section 3.5; page 484, Section 3.7; page 487, Section 3.8; page 494, Section 3.13; page 506, Section 3.22; and page 514, Section 3.24; and page 515, Section 3.25.

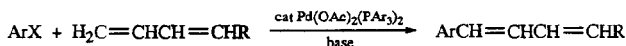




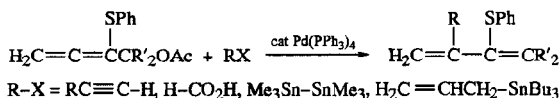
JOC 53 5588 (1988) (intramolecular); 54 2047, 4738 (chiral, intramolecular) (1989); 57 4690 (1992); 58 5583 (1993); 59 2685 (1994) (intramolecular)
 IACS 111 8932 (1989); 116 11737 (1994) (chiral, intramolecular)
 TL 32 1695 (1991) (intramolecular); 33 2589, 2593 (1992) (both chiral, intramolecular); 34 2505, 4965 (chiral, intramolecular); 5209 (1993); 35 6495 (1994) (intramolecular)
 SL 349 (1992); 785 (1993); 761 (1995) (intramolecular)



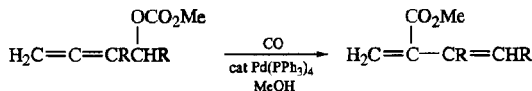
JOC 56 3486 (1991)



JOC 43 5018 (1978)
 Pure Appl Chem 53 2323 (1981)
 TL 33 1989 (1992)



SL 869 (1992)

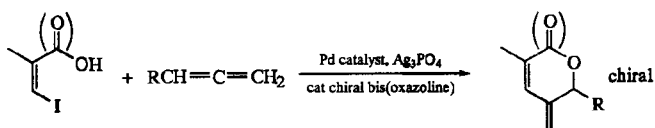


TL 31 5629 (1990)

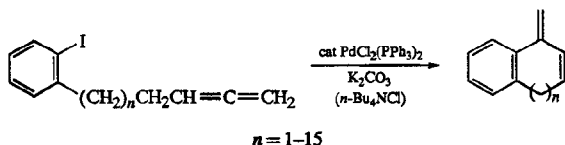


X = Br, I, O₃CCF₃; Y, Z = COR, COR; COR, CO₂R; CO₂R,
 CO₂R; CO₂R, CN; CO₂R, SO₂R; CO₂R, N=CR₂

TL 29 627, 4089 (1988); 30 3963 (1989); 32 915, 1795 (1991); 35 2881 (1994) (intramolecular); 36 5015 (1995)

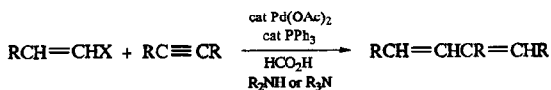


JOC 60 482 (1995)

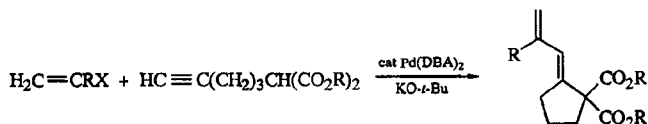


JOC 59 4730 (1994)

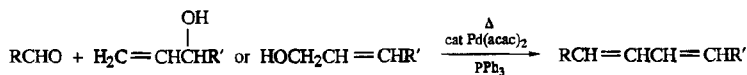
JACS 117 6345 (1995)



TL 29 4325 (1988) (intramolecular); 30 3465 (1989)

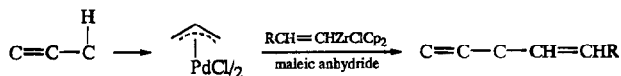


TL 31 5147 (1990)

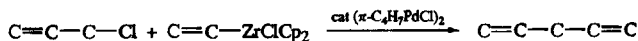


TL 22 3109 (1981)

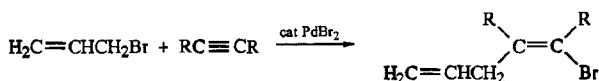
Syn Commun 16 1003 (1986)



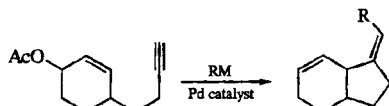
See page 494, Section 3.13.



See page 494, Section 3.13.

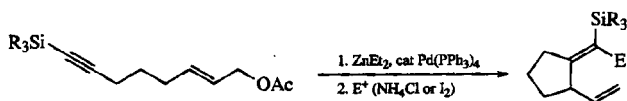
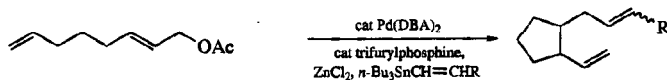


TL 29 5811 (1988)

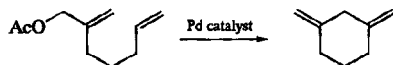


RM = NaBPh₄, PhZnCl, *n*-Bu₃SnCH₂CH=CH₂, NaO₂CH (R = H)

TL 32 2545 (1991)

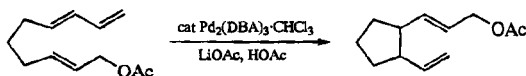


TL 35 7939 (1994)

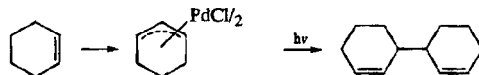


TL 29 4705, 4709, 5529 (1988); 30 291 (1989); 31 1265, 6877, 6995 (1990); 32 2161 (1991); 35 3333, 7939 (1994)

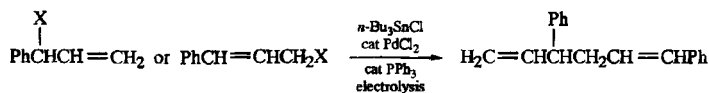
See page 499, Section 3.20.



JACS 110 8239 (1988)

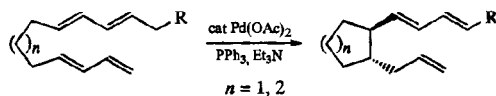


CC 258 (1980)

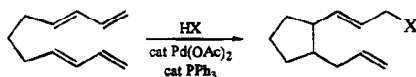


X = Cl, OAc

TL 27 4469 (1986)



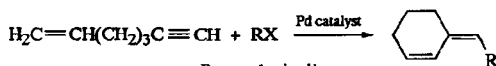
JACS 114 773 (1992)



HX = ROH, ArOH, R₂NH, RSO₂H, CH₃NO₂, H₂C(CO₂R)₂, (Et₃NH)OAc, enamine

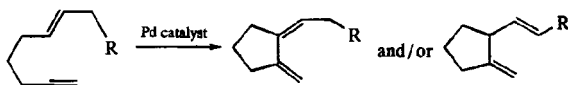
JOC 54 5193 (1989); 58 7315 (1993)

TL 31 1117 (1990); 35 9161, 9165 (1994)



R = aryl, vinylic

TL 34 19 (1993)



JACS 107 1781, 4586 (1985); 108 6053 (1986); 113 636, 670 (1991); 114 7292 (1992); 116 4255, 4268 (1994)

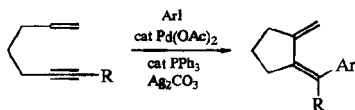
TL 26 4887 (1985); 28 1611 (1987); 30 651 (1989); 32 2161 (1991); 34 4735, 8233 (1993); 35 211, 9537 (1994); 36 5379 (1995)

JOC 54 2271, 4489 (1989)

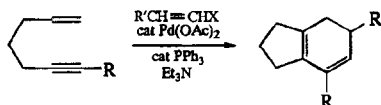
Acet Chem Res 23 34 (1990)

SL 539 (1993); 761 (1995)

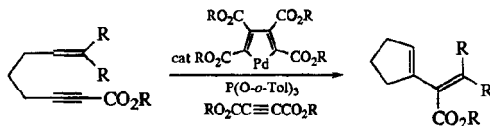
See page 499, Section 3.20, for a similar reaction.



JACS 114 1923 (1992)

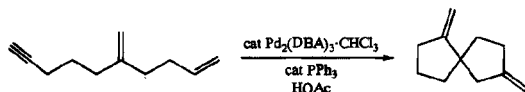


JACS 114 1923 (1992)

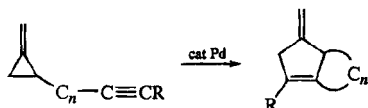


JACS 113 1850 (1991)

TL 32 3647 (1991)



JACS 113 701 (1991); 115 9421 (1993)

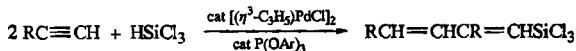


CC 948 (1988)

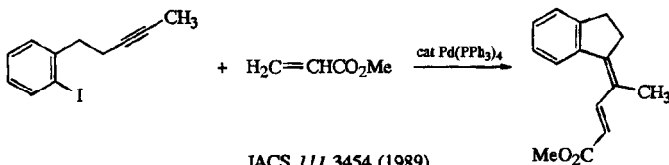
TL 30 7107 (1989)

JACS 116 8821 (1994)

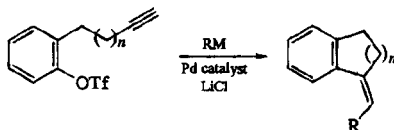
See also page 499, Section 3.20.



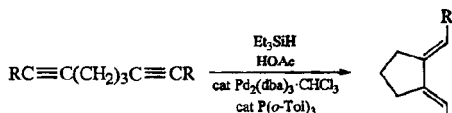
SL 1232 (1995)



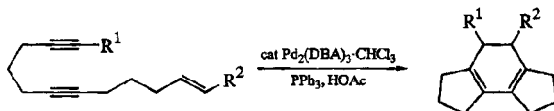
JACS 111 3454 (1989)

 $n = 1, 2$; $\text{RM} = n\text{-Bu}_3\text{SnCH}=\text{CH}_2$, $n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2$, $\text{H}_2\text{C}=\text{CHZnCl}$

TL 32 7703 (1991)



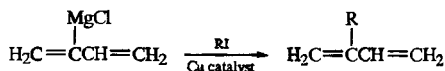
JACS 110 7255 (1988)



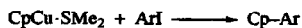
JACS 114 791 (1992); 115 12491 (1993)

3.22. Organocopper Compounds

See also page 452, Section 2.28; page 475, Section 3.1; page 476, Section 3.2; page 479, Section 3.4; page 482, Section 3.5; page 484, Section 3.7; page 487, Section 3.8; page 494, Section 3.13; page 514, Section 3.24; and page 515, Section 3.25.



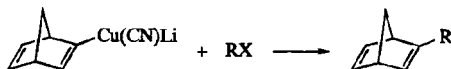
See page 476, Section 3.2.



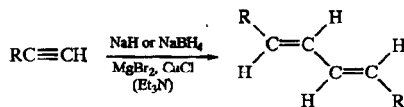
TL 30 2881 (1989); 31 4977 (1990)

JACS 115 3848 (1993)

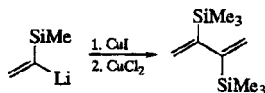
IOC 58 4078 (1993)



JOC 58 4122 (1993)

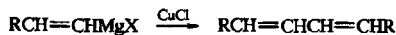


CC 495 (1987)



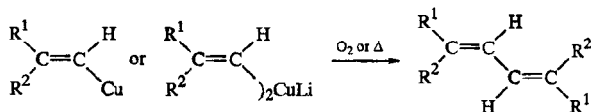
JACS 104 4299 (1982)

TL 27 2761 (1986); 29 1833 (1988)



Angew Int 6 85 (1967)

BCSJ 44 3063 (1971)



JACS 88 4541 (1966); 89 5302 (1967); 93 1379 (1971)

TL 2583 (1971); 29 1833 (1988)

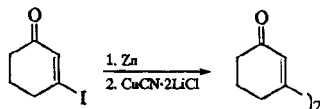
Angew Int 13 291 (1974)

JOMC 77 269 (1974)

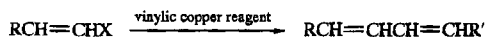
BSCF 1656 (1974)

Rec Trav Chim 95 299, 304 (1976)

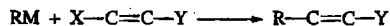
Organomet 1 667 (1982)



JOC 56 4593 (1991)



<u>X</u>	<u>Reagent</u>	
halogen	$(\text{R}'\text{CH}=\text{CH})_2\text{CuLi}$	JACS 91 6470 (1969) TL 191 (1978)
	$\text{C}_6\text{F}_5\text{C}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{Cu}$	JOC 60 4085 (1995)
OTf	$(\text{H}_2\text{C}=\text{CR})_2\text{CuMgBr}$	TL 21 4313 (1980) CC 1452 (1985)
	$(\text{H}_2\text{C}=\text{CH})_2\text{CuCN}(\text{MgBr})_2$	TL 28 3201 (1987)
	$\text{RCH}=\text{CHCu}$, cat $\text{Pd}(\text{PPh}_3)_4$	TL 32 5025 (1991)



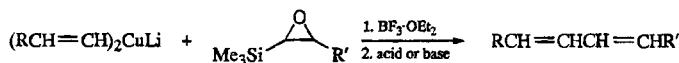
R = vinyllic

<u>X</u>	<u>Y</u>	<u>RM</u>	
PhSO_2	NO_2	$\text{RCu}(\text{CN})\text{ZnI}$	TL 32 441 (1991)
RTe	CO_2R	R_2CuZnCl or $\text{R}_2\text{Cu}(\text{CN})(\text{ZnCl})_2$	SL 180 (1995)



R'M

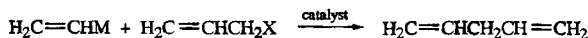
$(\text{RCH}=\text{CH})_2\text{CuMgBr}$	JOC 58 2296 (1993)
$\text{ThCu}(\text{CH}=\text{CHR})(\text{CN})\text{Li}_2$	TL 32 5647 (1991)
$(\text{RCH}=\text{CHCH}_2)_2\text{CuMgBr}$	JOC 58 2296 (1993)



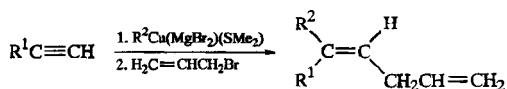
TL 29 217 (1988)



$(\text{RCH}=\text{CH})_2\text{CuLi} \cdot \text{SMe}_2$	TL 2705 (1978)
$\text{RCH}=\text{CHCu}(\text{CN})\text{ZnX}$	TL 31 4413 (1990) JACS 114 3983 (1992)



<u>M</u>	<u>X</u>	<u>Catalyst</u>	
MgX	OMs	CuCN	TL 32 855 (1991)
	O_2CR	CuCN	JOC 54 2369 (1989)
	$\text{OPO}(\text{OR})_2$	$\text{CuCN} \cdot 2\text{LiCl}$	SL 689 (1993)
AlR_2	$\text{OPO}(\text{OR})_2$	CuCN	SL 183 (1995)
ZrMeCp_2	$\text{OPO}(\text{OR})_2$	CuCN	SL 183 (1995)



TL 2583 (1971); 1363 (1978)

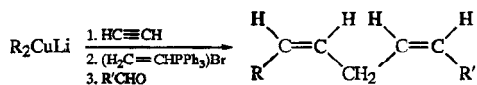
JOMC 40 C49 (1972); 77 269 (1974)

Syn 826 (1979)

JOC 44 3888 (1979)

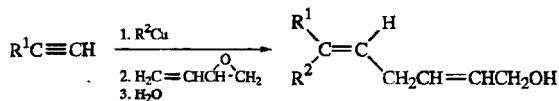
Org Syn 64 1 (1986)

Org Syn Coll Vol 7 236 (1990)



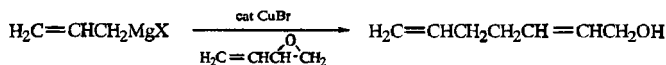
TL 26 1799 (1985)

JOC 52 1801 (1987)

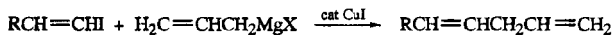


Syn 528 (1978)

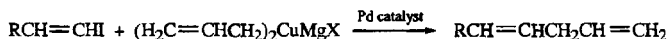
TL 2027 (1978)



Syn 528 (1978)



JOC 54 2817 (1989)



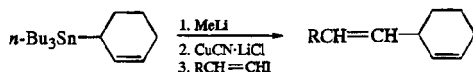
TL 36 2469 (1995)



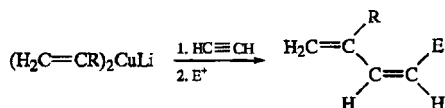
TL 32 157 (1991)



JOC 55 1695 (1990)



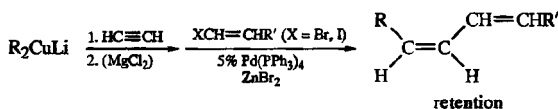
TL 31 4539 (1990)



$\text{E}^+ = \text{RI}, \text{CO}_2, \text{PhSCH}_2\text{NEt}_2$ ($\text{E} = \text{CH}_2\text{NEt}_2$)

BSCF 1656 (1974)

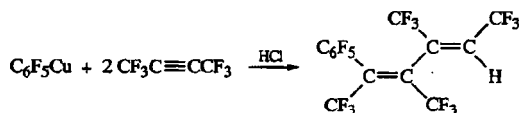
TL 23 5151 (1982)



TL 22 959 (1981); 23 1589, 5155 (1982)

BSCF II 321, 332 (1983)

Tetr 40 2741 (1984); 42 1369 (1986) ($\text{R}' = \text{COR}$)



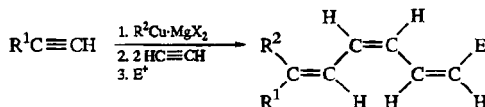
JOC 60 4085 (1995)



$\text{E}^+ = \text{R}'\text{X}, \text{enone}, \text{HC}\equiv\text{CCO}_2\text{Me}, \text{RCHO}, \text{CO}_2, \text{I}_2$

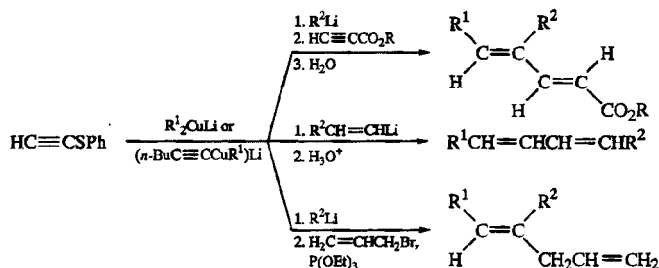
TL 26 2731, 3285 (1985)

JCS Perkin I 1809 (1986)

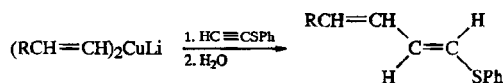


$\text{E}^+ = \text{RX}, \text{I}_2, \text{RCHO}, \text{CO}_2, \text{enone}, \text{HC}\equiv\text{CCO}_2\text{R}$

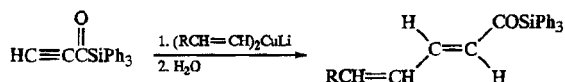
JCS Perkin I 1809 (1986)



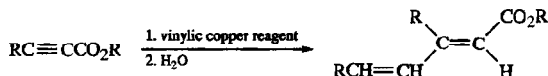
TL 35 6873 (1994)



TL 30 243 (1989)



SL 329 (1992)

Reagent $\text{RCH}=\text{CHCu}$

JACS 94 4395 (1972)

TL 1611 (1973); 3461 (1976); 23 5151, 5155 (1982)

Tetr 36 1961 (1980)

 $\text{RCH}=\text{CHCu}(\text{CN})\text{ZnX}$

JACS 114 3983 (1992)

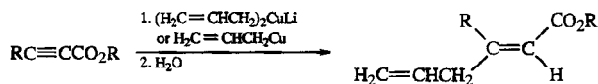
 $(\text{RCH}=\text{CH})_2\text{CuLi}$

Helv 54 1939 (1971)

JACS 94 4395 (1972); 99 7365 (1977)

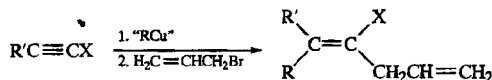
 $(\text{RCH}=\text{CRCu}\equiv\text{CCMe}_2\text{OMe})\text{Li}$

JACS 108 5559 (1986)



JACS 94 4395 (1972)

TL 1811 (1979)

R'XRCu

H

COSiPh₃*n*-Bu₃Sn(*n*-Bu)-
Cu(CN)Li₂

SL 332 (1992)

CF₃CF₃C₆F₅Cu

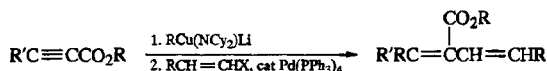
JOC 58 4411 (1993)

R

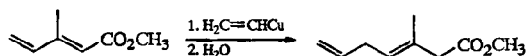
COR

(MeCuC≡CR)Li

JOC 48 4621 (1983)



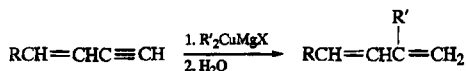
JOC 53 607 (1988)



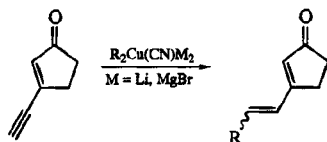
Helv 55 82 (1972)

JACS 94 4395 (1972)

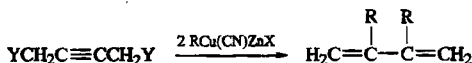
TL 1611 (1973)



JOMC 144 13 (1978)



TL 29 5851 (1988)

Y = Cl, OTs; R = 1°, 2° alkyl; ArCH_2 ; Ar

TL 32 2865 (1991)



Tetr 40 3645 (1984)



Gazz Chim Ital 112 415 (1982)



ArMgX, cat CuX (X = Cl, I, CN)

JOC 55 2757 (1990)

RMgX, Li_2CuCl_4

TL 28 1175 (1987)

JOC 56 7313 (1991)

 R_2CuLi

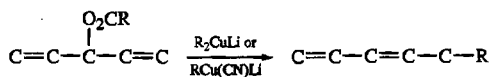
JOC 53 1140 (1988); 54 2369 (1989); 55 2757 (1990); 56 2563 (1991)

 $\text{RCu}(\text{CN})\text{Li}$

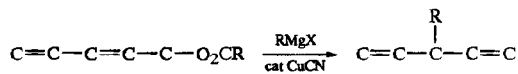
JOC 53 1140 (1988); 54 2369 (1989); 55 2757 (1990); 56 2563 (1991)

 R_2CuMgX

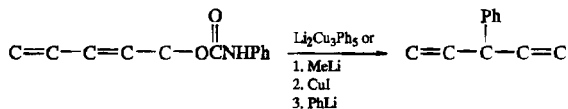
JOC 56 3278 (1991)



JOC 56 2563 (1991)



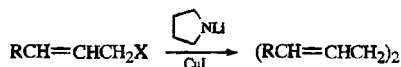
JOC 55 2757 (1990)



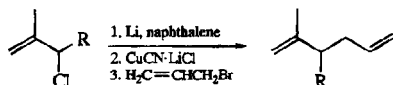
JOC 54 3239 (1989)



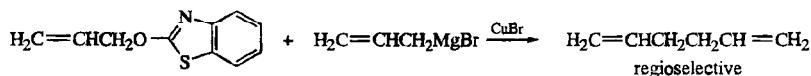
JOC 56 3279 (1991)



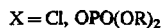
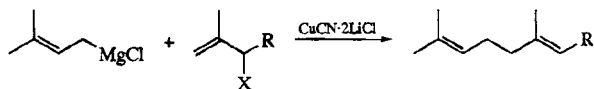
TL 783 (1979)



JACS 114 5110 (1992)



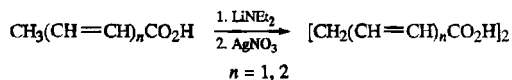
CC 1358 (1985)



SL 251 (1991); 689 (1993) (catalytic Cu)

3.23. Organosilver Compounds

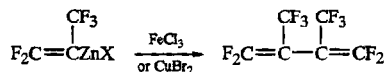
See also page 460, Section 2.29, page 475, Section 3.1; and page 484, Section 3.7.



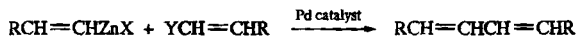
TL 29 6181 (1988)

3.24. Organozinc Compounds

See also page 460, Section 2.30; page 501, Section 3.21; and page 506, Section 3.22.



TL 32 4271 (1991)



Y

Br, I

Tetr 40 2741 (1984)

TL 27 4387 (1986); 29 6243 (1988); 30 6555 (1989); 31 2295, 4393 (1990); 32 3701, 4453, 6683, 6749 (1991); 33 511, 6139, 6839 (1992); 34 1437 (1993); 35 3089 (1994); 36 5413 (1995)

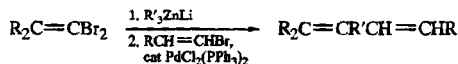
JOC 54 4727 (1989); 56 1445, 4593 (1991)

JACS 114 3983 (1992); 115 12621 (1993)

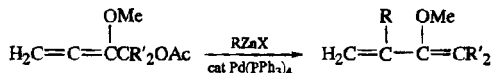
OTf

JOC 54 4727 (1989)

TL 31 1889 (1990); 32 4453 (1991)

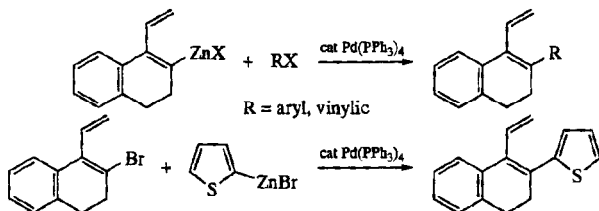


JOC 58 4897 (1993)

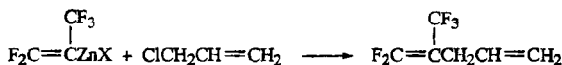


R = aryl, vinylic, alkynyl

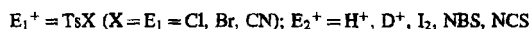
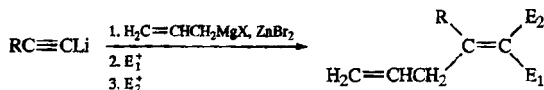
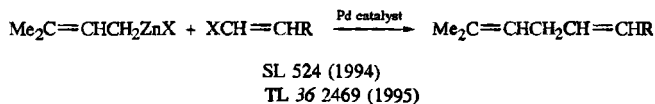
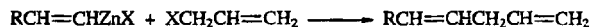
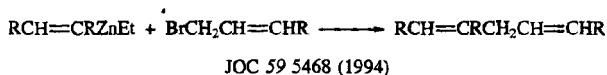
Rec Trav Chim 102 378 (1983)



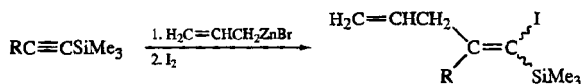
TL 28 1469 (1987)



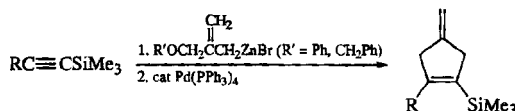
TL 32 4271 (1991)



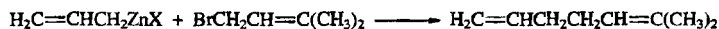
TL 36 7451 (1995)



JACS 116 932 (1994)

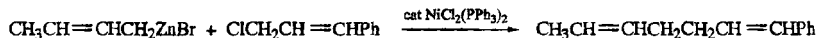


TL 28 2889 (1987); 30 4453 (1989)



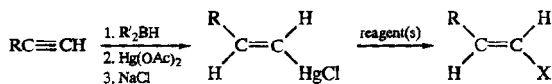
TL 24 1905 (1983)

JOC 57 5425 (1992)



TL 29 5156 (1988)

3.25. Organomercury Compounds



X

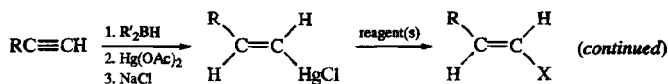
$\text{CH}=\text{CH}_2$



Reagent(s)

$(\text{H}_2\text{C}=\text{CH})_2\text{CuLi}$

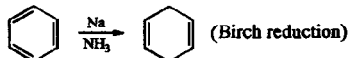
TL 22 3435 (1981)

Organomet 1 74 (1982)



<u>X</u>	<u>Reagent(s)</u>	
$\text{CR}=\text{CH}_2$	$\text{PdCl}_2, \text{C}_6\text{H}_6$	JOC 43 1468 (1978)
$\text{CH}=\text{CHR} \text{ (E)}$	cat $\text{Pd}(\text{PPh}_3)_4$	TL 3207 (1974)
	$\text{Li}_2\text{PdCl}_4, \text{HMPA}$	JOC 41 2241 (1976)
	cat $[\text{ClRh}(\text{CO})_2]_2$	JOC 42 1680 (1977)
$\text{CH}=\text{CHR}'$	$\text{R}'\text{CH}=\text{CH}_2$, cat LiPdCl_3 , CuCl_2	Bull Korean Chem Soc 7 142, 235, 472 (1986)
	$\text{R}'\text{CH}=\text{CH}_2, \text{Li}_2\text{PdCl}_4, \text{Et}_3\text{N}$	TL 35 1149 (1994)
	 , Li_2PdCl_4	TL 22 5231 (1981)
$\text{CH}_2\text{CH}=\text{CH}_2$	$\text{H}_2\text{C}=\text{CHCH}_2\text{Cl}, \text{Li}_2\text{PdCl}_4$	JOMC 156 45 (1978)

4. Arene Conversions



Reviews:

Quart Rev 4 69 (1950); I2 17 (1958)

Chem Rev 46 317 (1950)

"Steroid Reactions," Holden-Day, Inc., San Francisco (1963), pp 267-88, 299-325

"Organic Reactions in Liquid Ammonia, Chemistry in Non-Aqueous Ionizing Solvents," Wiley, New York (1963), Vol 1, part 2

"Reduction," Marcel Dekker, New York (1968), pp 95-170, 186-194

Syn 161 (1970)

Adv Org Chem 8 1 (1972)

H. O. House, "Modern Synthetic Reactions," Benjamin, Inc., Menlo Park, California (1972), pp 190-205

Natl Prod Repts 3 35 (1986)

Tetr 45 1579 (1989)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 3.4, p 489

Org Rxn 42 1 (1992)

Recent references:

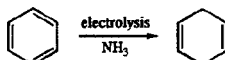
JOC 51 4983 (1986)

TL 29 3761 (1988)

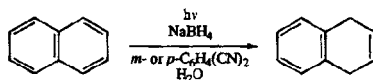
Org Syn Coll Vol 6 731, 996 (1988)

JACS 112 7299 (1990); 113 4288, 4926 (1991); 115 2205 (1993)

SL 344 (1993) (Li, NH_3 , *t*-BuOH or Li, McNH_2)

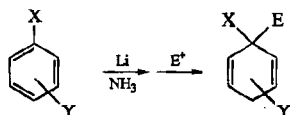


TL 28 1173 (1987)



JOC 46 788 (1981)

TL 27 1469 (1986)

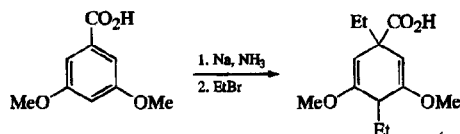


Reviews:

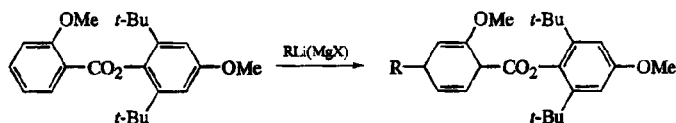
SL 134 (1991)

Org Rxs 42 1 (1992)

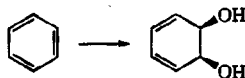
<u>X</u>	<u>E⁺</u>	
COR	RX	JOC 38 3887 (1973) JCS Perkin I 3214 (1981); 2399 (1983); 383, 735 (1985) CC 1292 (1986) TL 27 5253, 5303 (1986)
CO ₂ H(R)	RX	JOC 34 126 (1969); 41 2649 (1976); 42 1794 (1977); 45 1722 (1980); 49 4429 (1984); 50 915, 3086 (1985); 51 2844 (1986); 52 5482 (1987); 53 3210 (1988) Rec Trav Chim 90 137 (1971) JCS Perkin II 851 (1976) TL 2079 (1976); 21 3309 (1980); 22 3683, 4115 (1981); 23 1095 (1982); 24 1369 (1983); 27 1481, 3923 (1986) Austral J Chem 30 1045 (1977); 31 1157 (1978); 34 675 (1981) Ind J Chem B 16 1027 (1978) Syn 374 (1979) JACS 102 5085, 6628 (1980); 107 5574 (1985); 108 5893 (1986); 109 3991 (1987); 110 5547 (1988); 111 7507 (1989); 114 3937 (1992) Ber 114 214 (1981) Tetr 38 2831 (1982); 39 4221 (1983) (naphthalene) Nat'l Prod Repts 3 35 (1986) (review) CC 315 (1980)
	RCH=CHCO ₂ R (1,4-addition) (camphorsulfonyl)- oxaziridine (E = OH, enantioselective)	JOC 57 2973 (1992)
CONR ₂	H ⁺ RX	JACS 110 7828 (1988) (diastereoselective) JOC 51 4983 (1986) JACS 110 7828 (1988); 113 4931 (1991) (both diastereoselective) TL 36 4551 (1995)
CN	RX	JOC 51 4983 (1986) JACS 109 3991 (1987)



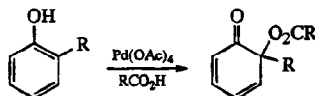
Syn Commun 11 223 (1981)



TL 36 4821 (1995)



See page 977, Section 2.

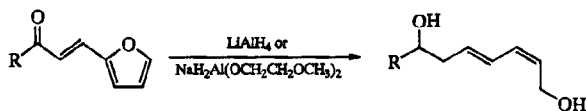


Monatsh 81 811, 1055 (1950)

Can J Chem 66 1 (1988)

JOC 55 5669 (1990)

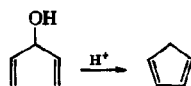
JACS 114 1790 (1992)



TL 31 5301 (1990)

5. Cyclization

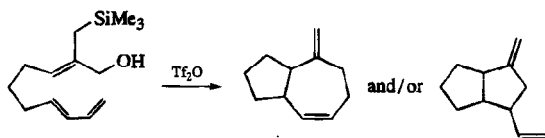
See also page 475, Section 3.1; page 484, Section 3.7; page 487, Section 3.8; page 492, Section 3.11; page 493, Section 3.12; page 494, Section 3.13; page 496, Section 3.15; page 497, Section 3.16; page 498, Section 3.17; page 499, Section 3.18; page 499, Section 3.19; page 499, Section 3.20; page 501, Section 3.21; page 514, Section 3.24; page 534, Section 19.1; and page 535, Section 19.2.



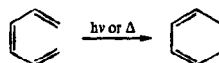
JACS 91 6404 (1969); 114 6942 (1992)

JOMC 136 1 (1977)

Org Syn Coll Vol 8 505 (1993)



TL 29 6071 (1988); 31 4577 (1990)



CC 173 (1970)

E. N. Marvel, "Thermal Electrocyclic Reactions," Academic Press, New York (1980) (review)

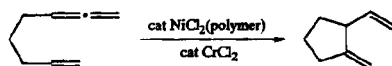
JACS 107 1034 (1985)

JOC 51 4131 (1986)

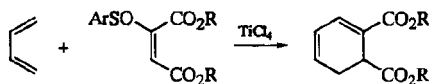
JCS Perkin I 225 (1987)

TL 28 1469 (1987); 30 6331 (1989)

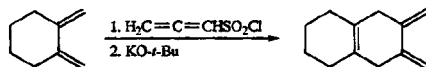
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol. 5, Part 6.2, p 699 (review)



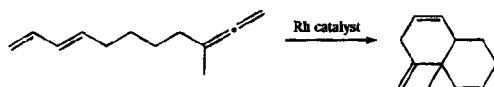
JACS 110 5231 (1988)



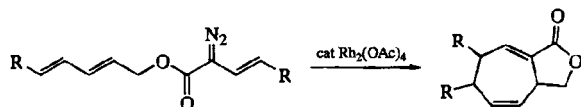
JOC 58 3231 (1993)



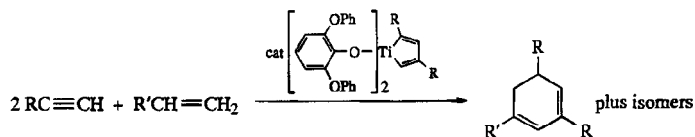
JACS 112 4072 (1990)



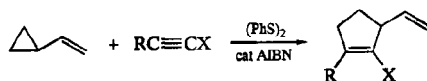
JACS 117 1843 (1995)



JOC 54 930 (1989)

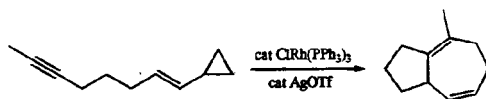


JACS 115 1580 (1993)

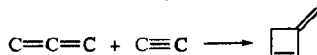
X = CO₂R, SO₂R

TL 30 5845 (1989)

JOC 56 4601 (1991) (intramolecular)



JACS 117 4720 (1995)

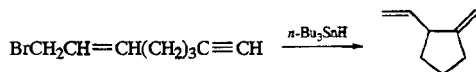


JCS C 2051 (1966)

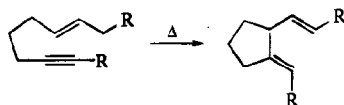
JCS Perkin I 1844 (1974)

J Chem Res (S) 136 (1977)

JOC 53 4807 (1988); 57 1146 (1992)



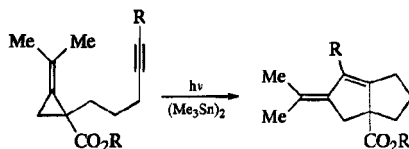
JACS 110 6911 (1988)



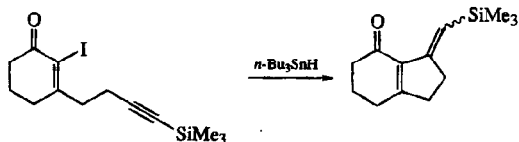
CL 2347 (1987)

SL 235 (1993)

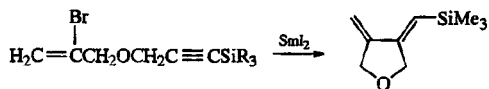
JACS 116 10948 (1994)



TL 35 691 (1994)

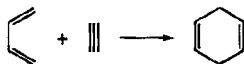


TL 34 7641 (1993)



TL 35 8445 (1994)

JOC 60 7424 (1995)

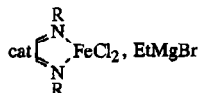
cat TiCl_4 , Et_2AlCl

JOMC 289 331 (1985)

cat FeCl_3 , $i\text{-PrMgCl}$

JOC 33 3948 (1968)

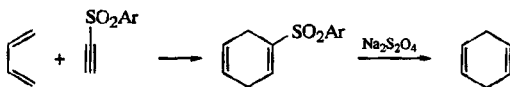
TL 1499 (1979)



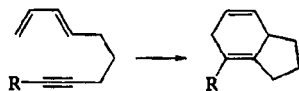
Angew Int 22 778 (1983)

cat $[\text{Rh}(\text{COD})(\text{dppb})]\text{PF}_6$

TL 28 3361 (1987)



JACS 112 8889 (1990)



TL 30 7157 (1989)

TL 30 7157 (1989)

cat $\text{Ni}(\text{COD})_2$

JACS 111 6432 (1989)

cat $\text{Ni}(\text{COD})_2$, cat $\text{P}(\text{O}-i\text{-C}_3\text{HF}_6)_3$

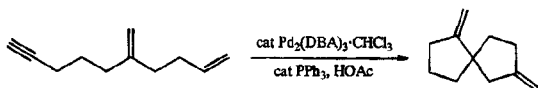
JOC 60 2962 (1995)

cat $\text{Ni}(\text{acac})_2$, cat Et_2AlOEt , cat $\text{P}(\text{O}-i\text{-C}_3\text{HF}_6)_3$

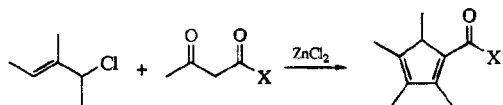
JOC 60 2962 (1995)

cat $\text{ClRh}(\text{PPh}_3)_3$ or $[(\text{RO})_3\text{P}]_2\text{Rh}^+$

JACS 112 4965 (1990)



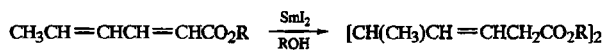
See page 501, Section 3.21.



X = Me, OR

TL 29 5641 (1988)

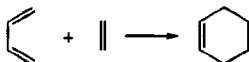
6. Miscellaneous Reactions



TL 32 6557 (1991)

8. DIELS-ALDER REACTIONS

For Diels-Alder reactions affording arenes, see page 207, Section 6.



1. General Reviews

- Org Rxs 4 1, 60 (1948); 5 136 (1949)
Chem Rev 61 537 (1961) (stereochemistry); 93 741 (1993) (acceleration and selectivity)
A. S. Onishchenko, "Diene Synthesis," D. Davey Co., New York (1964)
R. Huisgen, R. Grashey and J. Sauer, "The Chemistry of Alkenes," Ed. S. Patai, Interscience, New York (1964), Chpt 11
A. Wasserman, "Diels-Alder Reactions," Elsevier, New York (1965)
Angew Int 5 211 (1966); 6 16 (1967)
"1,4-Cycloaddition Reactions. The Diels-Alder Reaction in Heterocyclic Syntheses," Ed. J. Hamer, Academic Press, New York (1967)
Houben-Weyl, "Methoden der Organischen Chemie," Vol 5/1c, G. Thieme, Stuttgart (1970), p 977
Russ Chem Rev 58 230 (1989)
W. Carruthers, "Cycloaddition Reactions in Organic Synthesis," Pergamon, Elmsford, NY (1990)
F. Fringuelli and A. Taticchi, "Dienes in the Diels-Alder Reaction," J. Wiley & Sons, New York (1990)
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 4.1, p 315

2. Regioselectivity

Facial selectivity

- JACS 77 4183 (1955); 91 6129 (1969); 92 7385 (1970); 96 4671 (1974); 100 5845 (1978); 107 1971, 6598 (1985); 109 663 (1987); 110 4074, 4625, 6521 (1988); 111 2351, 5792 (1989); 112 1136, 2942, 8472, 8980 (1990); 113 246 (1991); 117 163, 5992, 9190 (1995)
TL 3723 (1973); 30 3897, 5077, 6405 (1989); 32 5935, 5939 (1991); 34 423, 8055 (1993); 35 2309, 2313 (1994); 36 4873, 6105 (1995)

- Tetr 29 3227 (1973); 39 2095 (1983)
Pure Appl Chem 51 1301 (1979)
CC 739 (1980); 1247 (1985)
Acct Chem Res 16 328 (1983)
JOC 51 3864 (1986); 52 3050, 4726, 4732 (1987); 53
1835 (1988); 56 997, 2542 (1991); 57 5585
(1992); 58 4979 (1993); 60 2328, 5931 (1995)
A. G. Fallis, Y.-F. Lu in "Advances in Cycloaddition," Ed. D. P. Curran, JAI Press, Greenwich, CT
(1993), Vol 3, pp 1-66
J. A. Coxon, D. Q. McDonald and P. J. Steel,
"Advances in Detailed Reaction Mechanisms,"
Ed. J. M. Coxon, JAI Press, Greenwich, CT
(1994), Vol 3, p 131
SL 801 (1994)
- Frontier orbitals JACS 95 4092 (1973); 108 7381 (1986)
Acct Chem Res 8 361 (1975) (review)
JOC 43 1864 (1978); 46 2338 (1981) (quinones)
Pure Appl Chem 55 237 (1983)
- Diene polarity JACS 100 7098 (1978)
TL 22 2043, 2047 (1981)
- Dienophile substituents JOC 47 5009 (1982)
JACS 114 1089 (1992)
- Lewis acids JACS 86 3899 (1964); 95 4094 (1973); 114 1089
(1992)
TL 5127 (1970)
Can J Chem 50 2377 (1972)
JOC 45 5012 (1980)

3. Exo/Endo Selectivity

- Angew 50 510 (1937) (review)
Chem Rev 61 537 (1961) (review)
TL 731 (1966); 29 3477 (1988); 30 5887, 5891 (1989); 32 3293 (1991); 33 1851 (1992)
JACS 92 6548 (1970); 93 4606 (1971); 94 3633 (1972); 114 1089 (1992); 116 12115 (1994)
JOC 47 3186 (1982) (microemulsions); 48 276 (1983); 56 1955 (1991)
SL 565 (1995)

4. Asymmetric Diels-Alder Reaction

4.1. Reviews

- L. A. Paquette in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984),
Chpt 7
Angew Int 23 876 (1984)
Tetr 42 5157 (1986)
"Modern Synthetic Methods 1986," Springer, New York (1986), p 261 (chiral enoates)

- M. J. Taschner in "Organic Synthesis: Theory and Application," Vol 1, Ed. T. Hudlicky, JAI Press, Greenwich, CT (1989)
Syn 1 (1991) (chiral catalysts); 535 (1994) (hetero Diels-Alder)
Org Prep Proc Int 26 129 (1994)
Houben-Weyl, "Methods in Organic Chemistry," 4th ed, Vol E21c, G. Thieme, Stuttgart-New York (1995), pp 2735-2952

4.2. Regular Diels-Alder Reaction

4.2.1. Functionality on C=C of chiral dienophile

Aldehyde

JOC 55 5477 (1990)

Ketone

JOC 48 1137, 4441 (1983); 57 6566 (1992)
TL 32 7465 (1991); 36 4893 (1995)

Monooester

Angew Int 4 489 (1951); 24 112 (1985)
JOC 31 2418 (1966); 53 1125 (1988); 57 3380, 5071 (1992); 60 364, 7230 (1995)
TL 6359 (1966); 26 1631, 3095 (1985); 28 183 (1987); 30 5595, 5599 (1989); 31 3563 (1990); 32 4557, 5529, 6839, 7043 (1991); 33 3323 (1992); 35 7451 (1994); 36 943 (1995)
JACS 97 6908 (1975); 115 10139 (1993)
CC 423 (1987)
SL 260 (1991); 421, 683 (1993)
Tetr Asym 4 2291 (1993)

Monoamide

JOC 53 6133 (1988); 56 6551 (1991)
TL 30 4227, 5891 (1989)

Imide

TL 32 5877 (1991)
JACS 114 2258 (1992)
JOC 57 1059 (1992)

Acyloxazolidinone

JACS 106 4261 (1984); 110 1238 (1988)
JOC 55 5065 (1990); 56 5758 (1991); 60 6847 (1995)
TL 32 7715 (1991); 33 4461 (1992); 35 489, 721 (1994); 36 7619 (1995)
Tetr Asym 4 629 (1993)

Sultam

Helv 67 1397 (1984)
TL 26 5437 (1985); 29 5885 (1988); 31 5015 (1990); 35 3509 (1994)
Tetr 42 4035 (1986)

Other monofunctional dienophiles

JOC 49 1527 (1984) (sulfoximine); 51 1457 (1986) (sulfoxide); 54 2428 (1989) (acylurea); 59 6890 (1994) (2-alkenal acetal)

CC 609 (1986) (acyl iron)
TL 30 1395 (oxazoline), 1893 (alkoxyiminium salt) (1989)
JACS 112 6672 (1990) (oxazoline)
Sulfur Reports 15 41 (1993) (sulfoxide)

Diesters

JOC 26 4778 (1961); 53 226 (1988); 58 4555 (1993)
Tetr 19 2333 (1963)
TL 27 4507 (1986); 28 5841 (1987); 32 6839 (1991)
JACS 114 1089 (1992); 116 6153 (1994)

Other di- or polyfunctional dienophiles

TL 27 5509 (1986) (3-sulfinyl-2-alkenoate ester); 28 107 (1987) (3-sulfinyl-2-alkenoate ester); 30 3853 (2-sulfinyl-2-alken-1-one), 4003 (sulfinyl quinone), 4227 (fumaric diamide), 6973 (2-alkoxycarbonyl-2-alkene-4-lactam), 6977 (2-alkoxycarbonyl-2-alkene-4-lactam) (1989); 32 947 (sulfinyl maleate), 2005 (2-acyl-2-alkenoate ester), 7751 (4-alkoxy-3-sulfonyl-2-alken-4-olide) (1991)
JOC 56 1983 (1991) (sulfinyl maleimide); 57 4664 (2-cyano-2-alkenoate ester), 6870 (sulfinyl quinone) (1992); 59 1499 (sulfinyl maleate), 2211 (1-nitro-2-sulfinyl-1-alkene), 7774 (2-cyano-2-alkenoate ester) (1994); 60 4962 (1995) (1,1-disulfinyl-1-alkene)

4.2.2. Chiral diene

JACS 102 7595 (1980); 110 3257 (1988); 112 6743 (1990); 113 7630 (1991)
TL 23 4875 (1982); 29 5225 (1988); 30 6227 (1989); 36 1283 (1995)
JCS Perkin I 1339 (1990)
JOC 59 3421, 4162 (1994)

4.2.3. Intramolecular Diels-Alder

JACS 104 2269 (1982)

4.2.4. Chiral promoters and catalysts

Reviews

Syn 1 (1991)
Chem Rev 92 1007 (1992)
Org Prep Proc Int 26 129 (1994)

Lewis acids

CC 437 (1979) (Al)
TL 27 4895 (1986) (B); 28 777 (B), 5687 (Al) (1987); 30 7231 (1989) (B, intramolecular); 32 883 (Ti), 6289 (Ti), 7517 (Al) (1991); 33 6807 (1992) (Mg, Fe); 34 123 (Fe), 3979 (B), 4535 (Yb), 7027 (Cu), 8399 (Ti) (1993); 35 6325 (Yb, Sc), 7209 (B) (1994); 36 221 (B), 3321 (B), 5031 (Mg) (1995)
JACS 108 3510 (1986) (B); 111 5340 (Ti), 5493 (Al) (1989); 113 728 (Fe), 7794 (B), 8966 (B) (1991); 114 7938 (Al), 8290 (B) (1992); 115 3814 (Al), 6460 (Cu), 10412 (B) (1993); 116 1657 (B), 2812 (Ti), 3611 (B), 4083 (Yb), 12089 (Al) (1994); 117 9616 (1995) (Al)
CL 1109, 1967 (1986) (both Ti)
JOC 54 1481 (1989) (B); 57 396 (Ti), 2987 (B); 58 2938 (Ti), 6917 (B) (1993); 59 3758 (1994) (Sc); 60 1777, 1788 (1995) (both Ti)
SL 194 (B), 197 (B, Al, Ti) (1990); 829 (Mn), 967 (Ti) (1995)

Protic acid

JACS 116 1561 (1994)

Bovine serum albumin

TL 29 3347 (1988)

Catalytic antibodies

JACS 117 7041 (1995)

Chiral base

TL 30 7403 (1989)

Chiral photosensitizer

JACS 112 9635 (1990)

Chiral solvent

JACS 115 8780 (1993)

4.3. Inverse Electron-Demand Diels-Alder Reaction

Chiral dienophile

TL 27 667 (1986); 28 2681 (1987); 30 5347 (1989); 32 3147 (1991)

JACS 108 7373 (1986)

Chiral diene

CC 1786 (1985)

Chiral catalyst

TL 35 2771 (1994)

4.4. Hetero Diels-Alder Reaction

Chiral dienophile

CC 540 (1983) (RCHO)

TL 24 3451 (1983) (RCHO); 30 7061 (1989) (RCONO); 31 2603 (1990) ($\text{RO}_2\text{CCH}=\text{N}^+\text{HR}$); 36 6399, 7535 (1995) (both RCONO)

Tetr 42 5045, 6477 (1986) (both RCHO)

Chiral diene

TL 28 4045 (1987)

Intramolecular

Angew Int 24 784 (1985)

TL 32 4325 (1991); 33 7161 (1992)

Chiral catalysts

CC 676 (1987) (Al, En)

JACS 110 310 (1988) (Al); 116 10520 (1994) (H, B)

IOC 57 1951, 3264 (1992) (both B); 60 5757 (1995) (Cu)

5. Mechanism

Angew Int 6 16 (1967); 19 779 (1980) (both reviews)

JOC 37 2181 (1972) (diradical)

JACS 95 4092, 4094 (1973) (concerted); 106 203 (1984) (unsymmetrical transition state); 111 9078, 9172 (1989) (both transition state); 115 2936 (MO calculations), 5296 (concerted), 7478 (calculations) (1993)

6. Use of High Pressure

JACS 96 3664 (1974); 98 1992 (1976); 102 6893 (1980); 103 7007 (1981); 108 3040 (1986); 111 4125 (1989)
JOC 42 282 (1977); 44 3347 (1979); 50 2576, 3239 (1985); 53 5460, 5464 (1988); 56 4135 (1991); 60 4617 (1995)

Chem Rev 78 407 (1978) (review)

BSCF II 461 (1978)

Heterocycles 16 1287, 1367 (review) (1981)

Helv 65 1021 (1982)

TL 23 2611, 4875 (1982); 26 2229 (1985); 27 1015 (1986); 28 4045, 5267 (1987); 29 4233, 5017, 5397, 5975 (1988); 30 1045, 5073 (1989); 32 6445 (1991); 35 73, 1189, 4843 (1994)

Syn Commun 13 537 (1983)

Tetr 42 5045, 6477 (1986)

SL 355, 1165 (1995)

7. Microwave Irradiation

TL 27 4945 (1986); 32 2363 (1991)

JOC 56 6968 (1991); 58 950, 2186 (1993)

8. Ultracentrifugation

TL 28 707 (1987)

9. Use of Ultrasound

JACS 111 1522 (1989)

JOC 55 4995, 5008, 5013 (1990)

10. Catalysis

Photolysis

JACS 106 6870 (1984); 108 8021 (1986); 112 9635 (1990) (enantioselective); 114 9309 (1992) (enantioselective)

TL 27 911 (1986); 29 5125 (1988)

JOC 54 3, 2549, 4881 (1989); 56 7313 (1991)
SL 275 (1990)

Salt effects

JACS 113 4340 (1991)
JOC 59 4612 (1994)

Antibodies

JACS 111 9261 (1989); 112 7430 (1990)
JCS Perkin I 1925 (1993)
Science 262 204 (1993)

Base

TL 36 5939 (1995)

Alumina

TL 32 2303 (1991)

Silica

TL 29 175 (1988)

Clay

TL 32 2905 (1991)

Protic acids

JOC 45 3461 (1980); 49 4674 (1984)
JACS 103 4948 (1981)
TL 35 2663 (1994)

Lewis acids

JOC 45 3461 (1980)
JACS 104 2269 (1982)
TL 32 1549 (1991); 35 231 (1994); 36 2645 (1995)
SL 565 (1995)
See also page 523, Section 2.

Metal perchlorates

JACS 112 4595, 9436 (1990) (both Li); 113 2761 (1991) (Li); 115 8002 (Li, Na, Mg, Ba), 11600 (Mg) (1993)
TL 34 7367 (1993) (Li); 35 2663, 6783 (1994) (both Li); 36 4447 (1995) (Li)
JOC 59 4612 (1994) (Li, Na, Mg, Ba)
SL 1155 (1995) (Li)

Various metal reagents

JACS 111 6070 (1989) (Mo, W, Fe); 112 4965 (1990) (Rh, intramolecular); 114 5464 (Ti), 6392 (Ru) (1992)
TL 30 1357 (1989) (Fe); 32 5299 (1991) (Fe); 33 6815 (1992) (Yb); 34 3755 (Sc), 3833 (Fe), 4535 (chiral Yb), 6460 (chiral Cu), 6777 (LiBF₄) (1993); 35 2545 (Sm), 2767 (Eu), 2771 (chiral Yb), 4843 (Sc) (1994); 36 3513 (1995) (Fe)
Organomet 10 2092 (1991) (Zr)

11. Solvent Effects

JACS 102 7816 (1980); 110 5613 (1988); 113 4241, 7430 (1991); 114 5440 (1992); 115 8780 (1993) (theory, asymmetric)
TL 24 1897, 1901 (1983); 25 1239 (1984); 29 3347, 3477, 3745 (1988); 30 1785 (1989); 35 1189 (1994); 36 2645 (1995)
JOC 48 3137 (1983); 52 1001 (1987); 59 5372 (1994); 60 3731 (1995)
SL 186 (1990) (review, intramolecular)

12. Retro-Diels-Alder Reaction

Angew Int 5 211 (1966) (review); 25 414 (1986) (review)
Chem Rev 68 415 (1968) (review)
Tetr 34 19 (1978)
TL 22 4553, 4557 (1981); 23 5463 (1982); 25 3459, 3461 (1984); 26 2103 (1985); 27 3045, 6295 (1986); 28 183, 357, 1329, 3027, 3147, 5819, 6503, 6507 (1987); 29 2365, 2757 (1988); 30 6607 (1989); 31 3783 (1990); 33 1909 (1992); 34 3885 (1993); 35 2787 (1994); 36 1685, 4661 (1995)
JOC 47 598 (1982); 49 1033, 4091 (1984); 51 2851 (1986); 52 4603, 5746 (aza) (1987); 53 1334, 4412, 4859 (1988); 54 1018, 6008 (1989); 55 1034, 2271 (1990); 57 5019 (1992); 58 2953, 6701 (1993); 60 6670 (1995)
JACS 106 4862 (1984); 108 1019 (1986); 109 5859 (1987) (aza); 110 7984 (1988) (enols)
Can J Chem 62 2019 (1984)
Syn 121 (1985) (review); 207 (1987) (review)
Austral J Chem 38 1339 (1985)
Syn Commun 15 959 (1985)
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 4.5, p 551
SL 191, 601 (1993); 1239 (1995)

13. Intramolecular Diels-Alder Reaction

Reviews:

Ann Rep Med Chem 9 270 (1974)
Angew Int 16 10 (1977)
Syn 793 (1978) (*o*-quinodimethane)
Chem Rev 80 63 (1980)
Chem Soc Rev 9 41 (1980)
Can J Chem 62 183 (1984)
Org Rx 32 1 (1984)
D. F. Taber, "Intramolecular Diels-Alder and Alder Ene Reactions," Springer, New York (1984)
Acct Chem Res 18 16 (1985) (imino)
Russ Chem Rev 55 1145 (1986)
SL 1 (vinylallenes as dienes), 186 (substituent and solvent effects) (1990); 873 (1995) (RCONO)

- W. R. Roush in "Advances in Cycloaddition," Vol 2, Ed. D. P. Curran, JAI Press, Greenwich, CT (1990)
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 4.4, p 513
Pure Appl Chem 64 1831 (1992)

Pertinent references:

- JACS 100 6289, 8034 (1978); 102 6353 (1980); 103 2090, 4948, 5200, 6261, 6696 (1981); 104 1033, 1140, 2269, 3216, 4725 (isobenzofuran as diene), 5708 (bridgehead alkene synthesis), 5715 (bridgehead enol lactone synthesis), 5719, 5728, 5853 (1982); 105 3732 (1983); 106 1133, 6085 (acid catalyzed), 6422, 6735, 7641, 8327 (1984); 107 2149, 2573, 4072, 4791 (1985); 108 4953 (1986); 109 447, 1186, 4390, 6124 (1987); 110 860, 1232, 2186, 3670, 3672, 8250 (1988); 111 3717, 5312 (allene), 5469, 6257 (1989); 112 4609, 8623, 8627 (1990); 113 224, 382, 4241 (1991); 114 2260, 3044, 7578 (1992); 115 2248 (imine), 2268, 4497, 12305 (1993); 117 1049, 9369 (1995)
- JOC 45 3461, 4264, 4267 (1980); 46 1506, 1509, 2273, 3763 (1981); 47 180, 337, 610 [via bis(orthoquinone)], 1789, 2682 (vinyl allene as diene), 4337 (pyrone as diene), 4611, 4786, 4825 (1982); 49 4674 (1984); 50 725 (bridgehead dienes), 1770, 2626, 2719, 2807, 3086 (1985); 51 1150, 1155, 1633, 2487, 3075 (ionic), 3553 (iminium ions), 3740, 4023 (1986); 52 564, 1236, 1638, 2040, 4369, 4661, 5548, 5700 (1987); 53 231, 318, 710, 1862, 2665, 3325 (immonium ion); 3658 (immonium ion), 3663, 5586 (1988); 54 265, 434, 915, 2425, 4114, 4239, 4335, 4695 (1989); 55 1270, 2398, 2725, 3431, 3912, 5278, 5766, 6236 (1990); 56 642, 1192, 2311, 2826, 2960, 3595, 4569, 6729, 6981, 7313 (1991); 57 1065, 2876, 4098, 4380, 5342, 5596 (1992); 58 516, 2068, 2186, 2381, 3840, 3928, 6083 (RCONO) (1993); 59 1358 (RCONO), 1621, 2010, 3752, 5596, 5977, 6879, 7197 (1994); 60 844, 977 (ionic), 4617, 4629, 5537, 5560, 5785, 6168, 7215, 7796 (1995)
- Helv 64 478, 1387 (1981); 65 2212 (1982)
- TL 22 97, 101, 361, 3929, 3933, 4877 (benzyne), 5141 (1981); 23 303, 1523, 2361 (1982); 24 3295, 3701 (1983); 25 19 (1984); 26 591, 1249, 2229, 2689, 3307, 5109, 5437 (asymmetric) (1985); 27 1837, 3045, 3227, 4877, 6291 (PhNMe₂ as solvent), 6295 (1986); 28 735, 927 (cation radical), 931, 1059, 1175, 2087, 2447, 2937, 2969, 3423, 3819 (photochemical), 5249, 5253, 5255, 5339, 5895 (allene), 6035, 6253 (1987); 29 135, 481, 1137, 1367, 1641, 2107, 2429, 2493, 2685, 2757, 3187, 3541, 5017, 5605 (indoles), 5825 (furans), 5885, 6059 (furans), 6215, 6349, 6369, 6409, 6505, 6725 (1988); 30 433, 1045, 1241, 1349 (furan), 2585 (furan), 4045, 4551, 6559, 6607, 7231, 7297 (1989); 31 755, 2301, 3363, 3753, 5885, 6585, 7201, 7315 (1990); 32 125, 1145, 1183, 1549, 2387, 2629, 2715, 4091, 4095, 4325, 4371, 4439, 6477, 6481, 6583 (1991); 33 2765, 3519, 3813, 4073, 4417, 4581, 4695, 5061, 5217, 5221, 6165, 7161 (1992); 34 39, 1831, 3367, 4427, 5947, 6237, 7279, 8003 (1993); 35 595, 691, 1071, 1317, 2663, 3617, 3683, 3937, 3945, 5351, 5355, 5559, 5669, 5759, 6495, 6603, 6685, 6783, 7311, 7949, 8333 (furan), 9213 (RCONO) (1994); 36 687, 1015, 1019, 1051, 3473, 5379, 6853, 7177, 7515 (1995)
- CL 29 (1981)
- Angew Int 21 620 (1982) (allene + arene); 24 784 (1985) (asymmetric, heterodienophile)
- Ann 973 (1982)
- Chem Pharm Bull 30 4000 (1982)
- CC 1423 (1984); 421 (1985); 671, 724, 1447, 1449, 1797 (solvent effect) (1986); 418, 898, 1449 (allenic ester), 1540, 1786 (1987)
- Can J Chem 66 1 (1988)
- JCS Perkin I 413 (1989)
- SL 279 (1990); 353, 472, 526, 854 (1991); 272, 275, 281 (hetero), 599, 757, 985 (1992); 399 (1993); 597, 647, 733 (1994); 105, 231, 355 (high pressure), 452, 513, 895, 909 (1995)
- Org Syn Coll Vol 8 353 (1993)

- TL 129 (1965) (1-oxa); 3417 (1977) (1-thia); 21 1133 (1980) (1-oxa); 25 721 (1984) (1-oxa); 26 5273 (1985) (1-oxa); 27 6181 (1986) (1-oxa); 28 4045 (1987) (1-oxa); 29 4799, 5855, 5913, 6115 (all 2-aza), 6349 (1-aza) (1988); 30 2481 (1-aza, 2-CN), 4449 (1-thia) (1989); 31 1697, 6629 (1990) (both 1-oxa); 32 125 (1991) (1-aza); 33 7161 (1992) (1-oxa); 34 4097 (1993) (2-aza); 36 2855 (1995)
- JOC 42 282 (1977) (1-oxa); 50 2719 (1-aza), 5678 (2-aza) (1985); 52 1638 (1987) (1-oxa); 53 810 (1-oxa, intramolecular), 3373 (1-oxa) (1988); 55 5439 (1-aza), 5646 (1-aza) (1990); 56 880 (1-aza), 2476 (1-oxa), 4098 (1-oxa), 4459 (2-aza) (1991); 57 3974 (1992) (1-aza); 58 2068, 2075 (1993) (both 1-aza)
- Tetr 39 2869 (1983) (aza review)
- Angew Int 24 784 (1985) (1-oxa, intramolecular, asymmetric)
- Ann 2261 (1985) (1-oxa)
- D. L. Boger, S. M. Weinreb, "Hetero Diels-Alder Methodology in Organic Synthesis," Academic Press, New York (1987) (general review)
- Adv Heterocyclic Chem 42 245 (1987) (review)
- CC 884 (1987) (1-oxa)
- SL 129 (1990) (2-aza review); 281, 755 (1992) (both 1-oxa)
- Org Prep Proc Int 22 315 (1990) (1-aza review)
- "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 4.3, p 451 (general review)
- Houben-Weyl, "Methods in Organic Chemistry," 4th ed, Vol E21c, G. Thieme, Stuttgart-New York (1995), pp 2905-2952 (enantioselective review)

19. Use of Substituted 1,3-Dienes

19.1. Heteroatom-substituted 1,3-dienes

Reviews:

- Syn 753 (1981)
- Acct Chem Res 14 400 (1981) (R_3SiO)
- F. Fringuelli, A. Taticchi, "Dienes in the Diels-Alder Reaction," J. Wiley and Sons, New York-Chichester (1990)
- Org Prep Proc Int 22 315 (1990) (1- or 2-RCONR)

Recent references:

- Helv 58 590, 593 (1975) (1-MeO₂CNR); 65 2563 (1982) (1,1-MeO, 3-Me₃SiO); 66 2769 (1983) (1-ArNH, 2-CO₂Me); 68 1133 (1985) (1-EtO, 4,4-Me)
- Chem Listy 70 1266 (1976) (1-R₂N)
- JACS 98 3027 (1-MeO, 3-Me₃SiO), 5017 (2-MeO, 3-PhS) (1976); 101 6996, 7001, 7008 (1979) (all 1-MeO, 3-Me₃SiO and derivatives); 102 3554 (1980) (2-RO or RCO₂, 3-RS); 103 2816 (1981) (1-RCONH); 104 2059 (1-PhS, 2-MeO, 3-Me), 2308 (1-AcO, 4-Me₃Si), 2923 (1-PhS, 2-Me₃SiO, 3-H or Me), 3511 (1-Me, 3-Me₃SiO) (1982); 105 6335 (1983) (1-RO₂CNH, 4-PhS or PhSO or PhSO₂) (1983); 109 6396 (1987) (2-PhSO₂, 4-H or Me); 111 4515 (1989) (chiral 1,1-OCH₂CHRO); 115 4403 (1-CH₂OR, 2-Me, 3-chiral amino), 6625 (2,3-R₃Sn) (1993)
- CC 681 (1976) (1-Me₃Si); 178 (1978) (1-Me₃Si; 1-Me₃Si, 3-Me₃SiO)
- JOC 41 2625 (1976) (1,4-AcO, 2-Me); 42 282 (1-AcO); 1819 (1-PhSe, 2-Me₃SiO, 4-MeO) (1977); 43 379 (1,1-MeO, 3-Me₃SiO), 2726 (2,3-Me₃SiO), 4559 (1-RCO₂, 4-Et) (1978); 46 1810 (1,3-Me₃SiO; 1-MeO, 3-Me₃SiO; 1,1-MeO, 3-Me₃SiO; 1,3-MeO, 1-Me₃SiO; 1-CH₂OR, 1,3-Me₃SiO; 1-Me, 4-MeO, 1,3-Me₃SiO), 4161 (2-MeO, 1,1,3-Me₃SiO; 3-Me, 1-MeO, 1-Me₃SiO; 1-Me, 1-MeO, 3-Me₃SiO; 1-Me, 1-Me₃SiO, 2-CO₂Me, 3-MeO; 1-Me, 1-MeO, 2-CO₂Me, 3-Me₃SiO) (1980); 47 2051 (2-Me₃SiO; 1-MeO, 3-Me₃SiO), 3649 (1-MeO, 3-Me₃SiO; 1-Me₃SiO; 2-Me₃SiO; 1-Me, 2-Me₃SiO; 2-Me₃SiO-1,3-cyclohexadiene), 4005 (1-PhS, 2-MeO), 4774 (1,3-MeO), 5009 (1-MeO, 3-Me), 5083 (1,4-MeO) (1982); 48 3096 (1,4-*t*-BuO), 4986 (1-MeO, 3-Me₃SiO, 2-H or Me), 5051

(1-PhS, 2-MeO; 2-PhS, 3-MeO; 2-ArS, 3-AcO or MeO; 1-PhS, 4-AcO) (1983); 49 1898 (1,4-*t*-BuMe₂SiO), 2954 (2-Cl or Br, 3-PhS or PhSe; 1,2-Cl, 3-PhS or PhSe; 1-Cl, 2-Br, 3-PhS or PhSe), 3595 (1-RO, 3-Me; 1-RO, 3-RSCH₂), 3628 (1-*t*-BuO, 3-Me₃SiO) (1984); 50 141 (2-PhS, 3-Me), 1955 (1,3-AcO; 1-EtO₂CO, 3-AcO) (1985); 51 2210 (2-Ph₂PO) (1986); 52 2334 (1987) (1-PhSe, 4-MeO); 53 1161 (1-RCONR), 2295 [2-OPO(OR)₂], 3020 (2-PhSO₂), 5305 (2-Ac, 3-PhS) (1987); 59 4367 (1994) (2-pyridinium)

TL 2113 (1976) (1,4-OCH₂O); 3323 (1978) (2-Et₃Si); 4537 (1979) (1-RCONR); 22 3381 (1981) (1-PhS, 2-RO, 3-Me); 23 775 (2-MeO), 2155 (1,3-MeO) (1982); 24 1171 (1983) (1-RO, 3-RSCH₂); 25 5715 (1984) (1-MeO, 4-CH₂CO₂Na); 26 381 (1-EtO, 1-*t*-BuMe₂SiO), 5175 (1-RO, 3-Me₃SiCH₂; 1-MeO, 3-Me₃Si; 2-Me₃SiCH₂), 6519 (1-MeO, 1-Me₃SiO, 3-MeO or Me₃SiO) (1985); 27 2761 (2,3-Me₃Si), 2913 (2-*n*-Bu₃Sn), 5075 (1-MeO, 3-Cl) (1986); 28 4169 (1987) [1-B(OR)₂]; 29 6719 (1988) (1-R₃Si, 4-PhS); 30 1907 (1-Me, 2-Me₃SiO), 2589 (2-PhSO₂), 3259 (2,3-ArSO₂), 3295 (1-RCONR), 3897 (1-RO), 5347 (2-PhSO₂) (1989); 31 845 (2H-thiopyrans), 1409 (1-O₂CX; X = OEt, NEt₂) (1990); 32 2197 (1-MeO, 4-Me₃SiO), 2517 (2-NO₂) (1991); 33 2965 (2,3-OC₆H₄O), 6147 (2-RCHOR', R' = H, R, SiR₃, Ac) (1992); 34 4587 (1,1-OCH₂CH₂O; 3-OSiR₃, -NR₂ or -SPh), 4827 [2-B(OR)₂], 6481 (1-MeO, 3-RSO) (1993); 36 6551 (2-Me, 1,3-morpholino), 8133 [1-RS, 2-OPO(OEt)₂], 8825 (1-Me₃Si, 2-PhS) (1995)

Org Syn 58 163 (1978) (2-Me₃SiO); 61 147 (1983) (1-MeO, 3-Me₃SiO)

JCS Perkin 1 1582 (1,1-RO), 2415 (1-Me₃Si; 1-Me₃Si, 3-Me or 3-Me₃SiO or 4-Me or 4-Me₃Si) (1981)

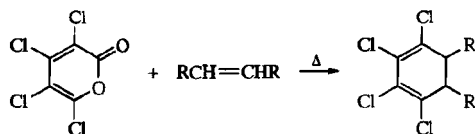
Tetr 37 4081 (1981) (1-MeO, 1-AcO, 3-Me₃SiO); 40 5039 (1984) (1-Me₃SiO, 1,2-MeO, 4-Me)

Syn Commun 11 481 (1981) (1,2-MeS); 14 797 (1-PhSeCH₂CH₂O, 3-Me) (1984)

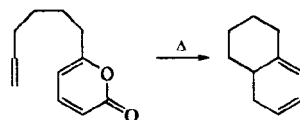
Syn 273 (1,4-EtO₂CNH), 380 (1,1,2,3-Me₃SiO); 958 (1-EtO₂CNH, 4-PhCO₂) (1982); 899 (1985) (2-*n*-Bu₃Sn; 2-PhMe₂Si)

CL 1057 (1982) [1-RO (R = *t*-Bu, Me₃Si, Ac), 3-Me₃SiO]

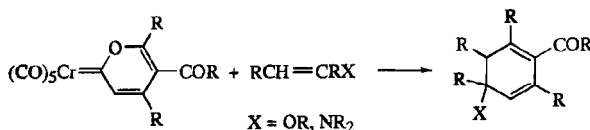
Can J Chem 62 2676 (1984) [2-OPO(OEt)₂, 4-Me]



JACS 109 7074 (1987)



JACS 109 6124 (1987)



JACS 112 4550 (1990)

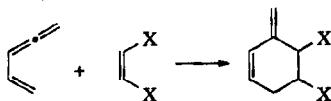
19.2. Carbon-Substituted 1,3-Dienes

Selected dienes

JOC 47 2051 (1982) (2-Me₃SiCH₂)

JACS 104 4299 (1982) (2,3-Me₃SiCH₂)

TL 23 551 (1982) (2-Me₃SiCH₂); 26 2555, 2559 (1985) (both 1-Ar or 1,2-Ar); 31 6201 (1990) (2-Me₃SiCH₂CH₂)
 Syn Commun 14 483 (1984) (2-COMe)



JCS 341 (1960)
 J Gen Chem USSR 32 3471 (1962)
 BCSF 962 (1971)
 Angew Int 14 501 (1975)
 JOC 43 1916 (1978); 47 2682 (1982) (intramolecular); 48 4370 (1983) (intramolecular); 49 5282 (1984) (intramolecular); 51 1199 (1986)
 CL 155 (1985)
 CC 647 (1985)
 JACS 108 7791 (1986) (intramolecular); 110 6432 (1988)
 SL 1 (1990) (review, intramolecular)

20. *o*-Quinodimethanes and Heterocyclic Analogues

Reviews:

Syn 793 (1978)
 Chem Soc Rev 9 41 (1980)
 Acct Chem Res 13 270 (1980)
 Heterocycles 14 1615 (1980)
 Pure Appl Chem 53 1181 (1981)
 Can J Chem 62 183 (1984)
 Org Prep Proc Int 23 237 (1991)

Intermolecular Reactions:

Helv 62 2017 (1979)
 CC 1119 (1979); 158, 430, 699 (1982)
 JACS 102 863, 6885 (1980); 103 476, 1992 (1981); 104 1106, 3511 (1982); 105 1586 (1983); 110 8483 (1988); 114 1157 (1992)
 Tet 37 3, 2547, 2555, 3813 (1981)
 TL 22 1357 (1981); 23 2973 (1982); 29 2329, 4959 (1988); 30 111, 2541, 3278 (1989); 31 1563, 3313, 6205 (1990); 32 5469 (1991); 33 1269, 7035 (1992); 34 1931, 7587, 8461 (1993); 35 417, 2035, 3975, 7505 (1994); 36 5371, 8307 (1995)
 JCS Perkin I 1383, 1386 (1981); 2239, 2249 (1982)
 JOC 47 2331 (1982); 51 3490, 4160 (1986); 52 28, 4833 (1987); 53 339, 5796 (1988); 55 3158, 4356, 4794 (1990); 57 1514, 5532, 5955, 6222 (1992); 58 4132, 4871, 5291 (1993); 59 4308, 6484 (1994); 60 588 (1995)
 Ann 1999 (1982)
 SL 333 (1990); 831 (1993)

Intramolecular reactions:

JOC 50 2764 (1985); 51 4749 (1986); 53 3663 (1988); 55 5625 (1990); 58 4298 (1993); 60 594, 2664 (1995)
 JACS 110 2931 (1988)
 SL 667 (1990); 89 (1991); 199 (1995)
 TL 35 9755 (1994)

Heterocyclic analogues:

- JACS *104* 1140 (1982) (indole)
 Acct Chem Res *17* 35 (1984) (indole)
 TL *28* 3303, 3423 (1988) (both indole); *29* 2689 (1988) (thiophene); *30* 7289 (1989) (indole); *31* 1487 (oxazole), 1491 (thiophene), 5197 (pyrazole) (1990); *33* 4201 (1992) (thiazole); *34* 6639 (1993) (pyrimidine); *35* 5293 (1994) (thiazole); *36* 2113 (pyridine), 3385 (indole), 5983 (quinoline), 6777 (quinoxaline) (1995)
 Chem Rev *89* 1681 (1989) (indole review)
 SI. 571 (*aza-ortho*-xylylene), 627 (benzofuran) (1991); 459 (1994) (furan)
 Reviews on Heteroatom Chemistry *8* 26 (1993) (review)
 JOC *58* 493 (1993) (pyrazole)

21. Arynes

- R. W. Hoffman, "Dehydrobenzene and Cycloalkynes," Academic Press, New York (1967)
 BCSJ *50* 3338 (1977)
 JACS *102* 6649 (1980) (bisaryne); *108* 4932 (1986); *110* 7178 (1988); *112* 8889 (1990); *117* 10595 (1995)
 JOC *46* 4874 (1981) (bisaryne); *51* 979 (1986) (bisaryne); *52* 792, 3835 (bisaryne) (1987); *54* 5667 (1989); *59* 1351 (1994); *60* 5770, 8278 (1995)
 TL *22* 4877 (1981) (intramolecular); *25* 2073 (1984) (bisaryne); *27* 5319 (1986); *29* 1687 (4,5-didehydropyrimidine), 1883 (intramolecular), 6227 (1988); *30* 5785 (1989); *32* 6735 (1991); *34* 5889, 8337 (1993); *35* 3805 (1994) (intramolecular); *36* 939, 7575 (2,3-didehydropyridine) (1995)
 Tetr *38* 427 (1982) (hetarynes review)
 Org Syn Coll Vol *6* 82 (1988)

22. Some Other Dienophiles

$R^1CH=CR^2CR^3(OR')_2$ (R^1, R^2 or $R^3 = H$ or Me; as allyl cation) JACS *109* 2182 (1987)

cyclopropenes

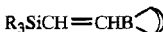


JOC USSR *12* 787 (1976); *14* 1132 (1978); *18* 1442 (1982)

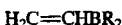
JACS *106* 440 (1984); *113* 4331 (1991)
 Chimia *40* 430 (1986)
 JOC *53* 1312 (1988)
 TL *30* 1507 (1989)
 Helv *73* 1228 (1990)

vinyl-9-BBN

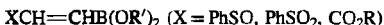
JACS *112* 7423 (1990)
 JOC *57* 5768 (1992)
 TL *33* 1017 (1992); *34* 3071 (1993)



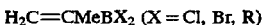
TL *32* 7365 (1991); *35* 509 (1994)



JOC *57* 5768 (1992)



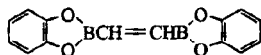
TL *30* 2929 (1989)



TL *34* 3071 (1993)

$\text{MeCH}=\text{CHBX}_2$ ($\text{X} = \text{Br}, 9\text{-BBN}$)

TL 34 3071 (1993)



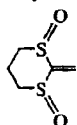
TL 35 509 (1994)

$\text{H}_2\text{C}=\text{CHC}(\text{OMe})=\text{W}(\text{CO})_5$

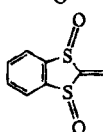
TL 35 557 (1994)

vinyl sulfonides

TL 27 6041 (1986)



SL 730 (1992)



SL 730 (1992)

$\text{PhSOCH}=\text{CHCO}_2\text{R}$

Austral J Chem 37 1677 (1984)

$\text{PhSOCH}=\text{CHNO}_2$

JOC 53 251 (1988)

$\text{PhSO}_2\text{CH}=\text{CHNO}_2$

JOC 53 251 (1988)

vinyl sulfones

TL 21 3339 (1980); 23 5127 (1982)

JACS 102 853 (1980)

JOC 48 4976, 4986 (1983)

E- or *Z*- $\text{PhSO}_2\text{CH}=\text{CHSO}_2\text{Ph}$

See page 541, Section 23, $\text{HC}\equiv\text{CH}$.

$\text{H}_2\text{C}=\text{C}(\text{SO}_2\text{Ph})_2$

Syn 757 (1984)

$\text{PhSO}_2\text{CH}=\text{CHCOR}$

TL 32 5405 (1991)

$\text{H}_2\text{C}=\text{CHNO}_2$

J Chem Res (S) 78 (1983)

$\text{RCH}=\text{CHNO}_2$

TL 30 3179 (1989)

$\text{PhCO}_2\text{CH}=\text{CHNO}_2$

TL 29 1879 (1988)

$\text{Me}_3\text{SiCH}=\text{CHNO}_2$

JOC 49 3235 (1984)

$\text{H}_2\text{C}=\text{C}(\text{O}_2\text{CR})\text{COCH}_3$

Helv 64 188 (1981)

JOC 47 409 (1982); 55 1024 (1990)

TL 28 865 (1987)

$(\text{MeO})_2\text{CHCH}_2\text{CH}=\text{CHCOCH}_3$

Can J Chem 60 2760 (1982)

cyclic enones

JOC 47 5056 (1982); 48 2802 (1983); 50 4686, 4691, 4696 (1985); 51 2642, 2649, 5177 (1986); 53 1424, 4607 (1988); 54 710, 1217 (1989); 56 387 (1991); 57 5771 (1992)

Tetr 41 349 (1985)

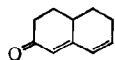
Org Prep Proc Int 22 131 (1990) (review)

TL 32 6445 (1991)

Acta Chem Scand 47 255 (1993) (review)

bicyclic enones

JOC 53 1397, 4325 (1988)



JOC 54 6138 (1989)



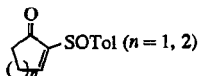
TL 23 841 (1982)



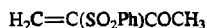
TL 23 841 (1982)



TL 29 6283 (1988)



TL 30 3853 (1989)

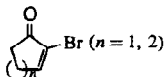


JOC 56 4098 (1991)

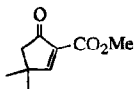


Can J Chem 57 377 (1979)

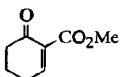
JOC 48 1810 (1983); 56 5353 (1991)



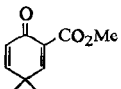
TL 36 1817 (1995)



TL 24 1353 (1983)



Syn Commun 12 715 (1982)



TL 2919 (1977)

Can J Chem 59 601 (1981)



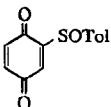
JOC 52 5298 (1987)



CC 837 (1983)

TL 29 5225 (1988); 33 6731 (1992)

JOC 53 4052 (1988); 59 1179 (1994)



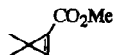
TL 30 4003 (1989)



JACS 110 6254 (1988) (chiral)



Angew Int 23 233 (1984)



JACS 111 4125 (1989)



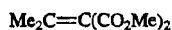
TL 30 571 (1989)



JACS 110 3965 (1988)



JOC 47 4152 (1982)



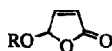
TL 32 355 (1991)



TL 32 7033 (1991)

butenolides

TL 5317 (1972); 25 19 (1984) (intramolecular); 27 1081 (1986); 28 3405 (1987); 29 6989 (1988)
CC 737 (1985)
JCS Perkin I 2279 (1986)



TL 31 3047 (1990)



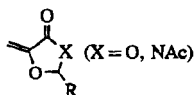
JOC 55 3060 (1990); 56 5567 (1991)



TL 31 4863 (1990)



TL 31 4859, 4863 (1990)



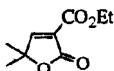
TL 30 7305, 7309 (1989)



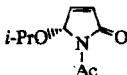
JOC 47 4777 (1982)



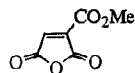
JOC 47 4152 (1982)



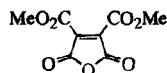
Can J Chem 60 921 (1982)



JOC 57 1059 (1992)



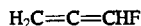
JOC 47 1451 (1982)



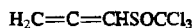
JOC 47 3647 (1982)



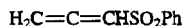
TL 30 3223 (1989)



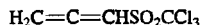
JACS 107 7183 (1985)



TL 35 6725 (1994)



JOC 50 512 (1985)



TL 35 6725 (1994)

allenic ketones

J Chem Res (S) 300 (1982)

allenic esters

Helv 65 2563 (1982)



JOC 57 4796 (1992)



JOC 55 1916 (1990)



CC 1452 (1984)



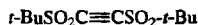
Ber 115 804 (1982)



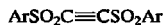
TL 29 831 (1988)



SL 1123 (1995)



TL 31 2173 (1990); 32 4579 (1991)



TL 32 2177 (1991)

5-membered aromatic heterocycles

JACS 110 7188 (1988)

23. Dienophile Equivalents

Equivalent

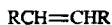
Reagent(s)



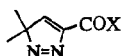
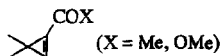
JACS 102 853 (1980)

JOC 48 4976 (1983)

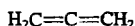
CC 451 (1986)



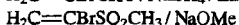
CC 33 (1982)



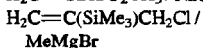
JACS 111 4125 (1989)



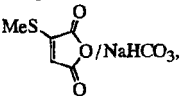
JOC 38 3961 (1973)



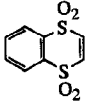



JACS 94 1012 (1972)



Organomet Chem Syn 1 253 (1971)

Equivalent	Reagent(s)	
$H_2C=C=CHR$	$(H_2C=CHPh)_3Br/LDA/$ RCHO	TL 2095 (1974) JOC 42 4095 (1977)
$H_2C=C=C=CH_2$	$H_2C=C=CHSO_2CH_2Cl/$ KO-t-Bu	JACS 112 4072 (1990)
$H_2C=C=O$	review $H_2C=CClCOCl/NaN_3/\Delta/$ H_3O^+ $H_2C=C(OAc)CN/base$	Syn 289 (1977) JACS 93 4326 (1971) JACS 78 2473 (1956); 82 627 (1960); 112 7682 (1990) JOC 31 3787 (1966); 46 4152 (1981) TL 121 (1972) CA 64 4965g (1966); 71 112496p (1969) JACS 91 5675 (1969); 93 1489 (1971) Ber 105 1840 (1972) TL 121 (1972) CC 642 (1974); 39 (1975) JOC 40 2565 (1975); 46 4152 (1981)
	$H_2C=CClCN/(S^{2-}), KOH$	TL 23 953 (1982)
	$H_2C=C(CN)N \text{ (cyclohexane ring)} O/hydrolysis$	TL 23 953 (1982)
	$H_2C=C(CN)SMe/hydrolysis$	TL 23 953 (1982)
	$H_2C=C(SMe)CO_2Me/$ hydrolysis	TL 23 953 (1982)
	$H_2C=CHCN/PCl_5/OH^-$	JOC 33 2111 (1968) CA 71 112496p (1969)
	$H_2C=CHB(OBu)_2/[O]$	TL 121 (1972)
	$H_2C=CHNO_2/NaOH/HCl$	JACS 96 5261 (1974) Tetr 32 961 (1976)
	$H_2C=CHCO_2H/LDA/O_2$	TL 4611 (1975)
	$H_2C=CHCO_2H/LDA/$ $(MeS)_2/NCS$	JACS 97 3528 (1975)
	$H_2C=CHSO_2Ar/LDA/$ MoO ₅ ·py·HMPA	TL 21 3339 (1980)
$MeO_2CCH=C=O$	$MeOC\equiv CCO_2Me/H_3O^+$ $PhSC\equiv CCO_2Me/H_2O, HgCl_2$ $BrC\equiv CCO_2Me/NaOMe/$ H_3O^+	CC 1227 (1982) CC 1227 (1982) TL 383 (1979)
	 $MeOH/NCS/H_3O^+$	JACS 99 7079 (1977)
$O=C=O$	$(H_2C=CHPh)_3Br/LDA/O_2$	TL 2095 (1974) JOC 42 4095 (1977)

	$\text{OC}(\text{CO}_2\text{Et})_2 / \text{OH}^- / \text{H}^+ /$ $\text{Pb}(\text{OAc})_4$ or Curtius	JACS 97 6892 (1975) JOC 42 4095 (1977)
$(\text{H}_2\text{C}=\text{CH})_2\text{CO}$	$\text{H}_2\text{C}=\text{CHCO}(\text{CH}_2)_2\text{Cl} / \text{bese}$ $\text{H}_2\text{C}=\text{CHCOCH}(\text{SePh})\text{CH}_3 /$ [O]	JACS 91 2806 (1969) Syn Commun 8 211 (1978)
$\text{HC}\equiv\text{CH}$	review	Tetr 40 2585 (1984)
	$\text{TsC}\equiv\text{CH} / \text{Na}(\text{Hg})$	CC 639 (1980) JACS 107 686 (1985)
	$\text{PhSOCH}=\text{CH}_2 / \Delta$	JACS 100 1597 (1978)
	$\text{XCH}=\text{CHX}$ (X = Cl, Br) / Zn or Na	JACS 74 2193 (1952) Tetr 28 3031 (1972)
	 -Ph / <i>n</i> -BuLi	CC 1593 (1968) JCS 886 (1971) JACS 95 7161 (1973) JCS Perkin I 2332 (1973)
	 =S / $\text{P}(\text{OMe})_3$, $\text{Fe}(\text{CO})_5$ or $\text{Ni}(\text{COD})_2$	JACS 85 2677 (1963); 95 7161 (1973) TL 2667 (1973) JOMC 69 423 (1974)
	<i>E</i> - $\text{PhSO}_2\text{CH}=\text{CHNO}_2 /$ <i>n</i> - Bu_3SnH	TL 27 1595 (1986) JOC 51 2139 (1986) JACS 111 4829 (1989)
	<i>Z</i> - $\text{PhSO}_2\text{CH}=\text{CHSO}_2\text{Ph} /$ Na(Hg)	CC 914 (1982) JOC 49 596 (1984); 52 3250, 4732 (1987); 54 3329 (1989); 57 4103 (1992) Can J Chem 62 2487 (1984) JACS 107 4789, 6400 (1985); 108 3453 (1986); 110 6521 (1988); 111 2351 (1989); 112 1159 (1990); 116 10883 (1994) TL 29 4069, 4213 (1988) TL 24 1653 (1983) Can J Chem 62 2487 (1984) JACS 107 6400 (1985) JOC 50 4340 (1985); 52 4740 (1987); 60 5770 (1995) Tetr 42 1789 (1986)
	<i>E</i> - $\text{PhSO}_2\text{CH}=\text{CHSO}_2\text{Ph} /$ Na(Hg)	
	 / Na(Hg)	Heterocycles 23 1119 (1985)
	<i>E</i> - $\text{PhSO}_2\text{CH}=\text{CHSiMe}_3 /$ <i>n</i> - Bu_4NF	TL 22 4643 (1981) JOC 48 4976 (1983)
	<i>Z</i> - $\text{Me}_3\text{SiCH}=\text{CHCO}_2\text{H} /$ electrolysis	Angew Int 23 233 (1984)
	$\text{ClCOCH}=\text{CHCOCl} /$ $\text{Pb}(\text{OAc})_4$	Syn 117 (1979)

<u>Equivalent</u>	<u>Reagent(s)</u>	
$\text{HC}\equiv\text{CH}$ (continued)	$\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me} / \text{NaOH} / \text{Cu}$	Tetr 28 3031 (1972)
	$\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me} / \text{NaOH} / \text{CuO}$	TL 4447 (1976)
	$\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me} / \text{NaOH} / \text{electrolysis}$	JACS 96 4671 (1974)
$\text{HC}\equiv\text{CR}$	$\text{NO}_2\text{CR}=\text{CHSO}_2\text{Ph} / n\text{-Bu}_3\text{SnH} \text{ or } \text{Na}_2\text{S}$	TL 27 1595 (1986)
	$\text{PhSO}_2\text{CH}=\text{C}(\text{Cl})\text{SO}_2\text{Ph} / \text{Et}_3\text{N} / \text{RMgX} / \text{Na}(\text{Hg})$	TL 30 1845 (1989)
$\text{HC}\equiv\text{CCOR}$	$\text{PhSO}_2\text{CH}=\text{CHCOR} / \text{NaOEt} \text{ or } \text{KO-}i\text{-Bu}$	TL 32 5405 (1991)
$\text{RC}\equiv\text{CR}$	$i\text{-BuO}_2\text{SC}\equiv\text{CSO}_2i\text{-Bu} / \text{RMgX}, \text{ cat Pd}(\text{acac})_2$	TL 32 4583 (1991)
$\text{N}\equiv\text{N}$	$\text{RO}_2\text{CN}=\text{NCO}_2\text{R} / \text{base} / [\text{O}]$	TL 2433 (1974)
	 $\text{NMe} / \text{KOH} / \text{CuCl}_2$	JACS 97 918 (1975) JACS 94 3658 (1972)

24. Transition Metal Carbenes as Dienophiles

JACS 105 6726 (1983); 106 7565 (1984); 110 2653 (1988); 112 3642 (1990)

JOMC 286 C23 (1985)

Angew Int 25 812 (1986)

JOC 51 3864 (1986)

CC 302 (1988) (intramolecular)

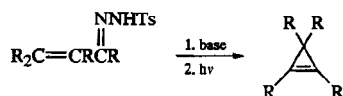
Organomet 7 2233 (1988)

Pure Appl Chem 60 137 (1988) (review)

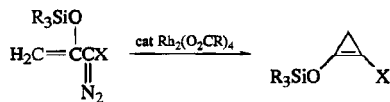
9. CYCLIZATION, ANNULATION AND RELATED REACTIONS

For cyclizations that annulate an alkene-containing moiety onto the carbon-carbon double bond of an enone, see also page 1329, Section 6.

1. Three-Membered Rings

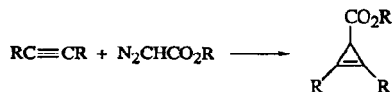


JOC 47 3377 (1982); 60 692 (1995)

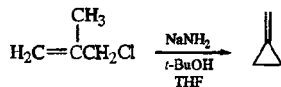


X = CO₂R, SO₂R, PO(OR)₂

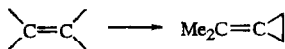
JOC 60 7529 (1995)



See page 410, Section 2.1; page 413, Section 2.2; and page 446, Section 2.23 for this and related reactions.



Org Syn Coll Vol 6 320 (1988)



Review: Chem Rev 78 383 (1978)

$\text{Me}_2\text{C=CHBr}$, KO- <i>t</i> -Bu	JOC 37 1553 (1972)
$(\text{Me}_2\text{C=CHPh})\text{BF}_4$, KO- <i>t</i> -Bu	JOC 60 2624 (1995)
$\text{Me}_2\text{C=CBr}_2$, MeLi	JOC 37 1553 (1972)
$\text{Me}_2\text{C=CHOTf}$, KO- <i>t</i> -Bu	JACS 97 6478 (1975)
$\text{Me}_2\text{C=CH(OTf)SiMe}_3$, R_4NF	Chem Rev 78 383 (1978)
$\text{Me}_2\text{C=CN}_2$	JOC 57 4185 (1992)
$\text{Me}_2\text{C=CHN=NAr}$	Chem Rev 78 383 (1978)



2. Four-Membered Rings

See also page 410, Section 2.1, and page 413, Section 2.2.

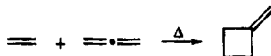


Thermal reactions

JCS 3880 (1955)
 JACS 84 4600 (1962); 86 1676 (1964); 87 3996 (1965); 88 1073, 4800 (1966); 89 112 (1967); 90
 3582, 5310 (1968); 92 399 (1970)
 JOC 30 3524 (1965)
 TL 3719, 3723 (1969)
 Tetr 25 4375 (1969)
 CC 1583 (1970)

Photochemical reactions

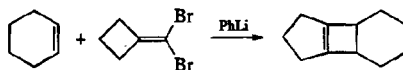
JOC 27 1910 (1962); 52 2644 (1987)
 JACS 84 1220 (1962); 88 2742 (1966); 94 4794 (1972); 97 2272 (1975)
 Proc Chem Soc 334 (1962)
 Chem Weekb 19 381 (1964); 21 1001 (1965)
 Rev Pure Appl Chem 16 117 (1966)
 Fortschr Chem Forsch 7 445 (1967)
 Adv Alicyclic Chem 2 185 (1968)
 Intra-Science Chem Reports, Vol 2 (1968)
 Org Syn Coll Vol 6 145 (1988)



See page 410, Section 2.1.

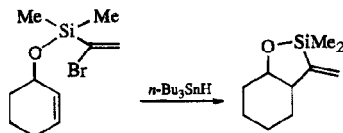


For photochemical ring closure, see page 413, Section 2.2, and for Lewis acid-catalyzed ring closures, see page 410, Section 2.1.



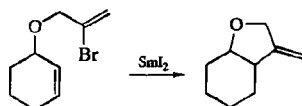
TL 23 1661 (1982)

3. Five-Membered Rings

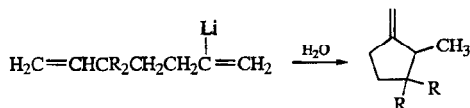


JACS 111 4984 (1984)

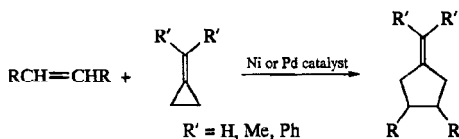
See also page 559, Section 8.



JOC 60 7424 (1995)



JOC 60 7791 (1995)



Angew Int 16 249 (1977); 21 622 (1982); 25 1 (1986) (review)

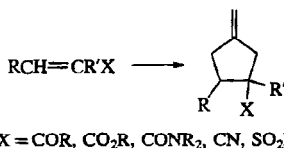
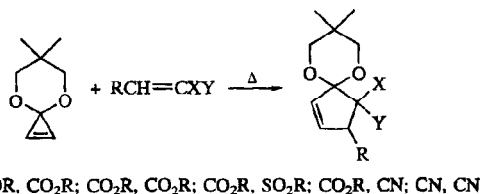
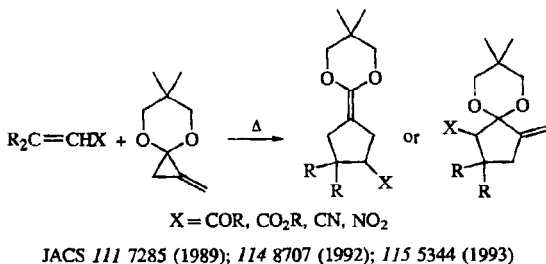
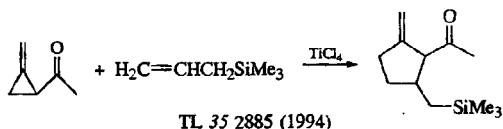
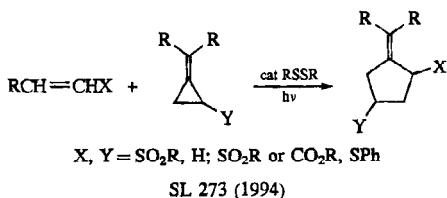
Ber 113 3334 (1980); 114 3313 (1981); 116 2920 (1983)

JOMC 221 C33 (1981)

TL 26 1045 (1985); 29 529 (1988); 32 1103 (1991) (intramolecular)

Topics Curr Chem 135 77 (1987) (review)

CC 1112 (1988) (intramolecular)

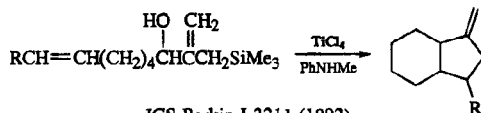


XCH₂C(=CH₂)CH₂SiMe₃, Pd catalyst (X = OAc, JACS 101 6429, 6432 (1979); 102 6359 (1980); 103 5972, 5974 (1981); 104 3733, 6668 (1982); 105 2315, 2326 (1983); 107 721, 1075, 1293 (1985); 108 284, 6051 (1986); 110 1602 (1988); 111 6482, OCO₂Me)

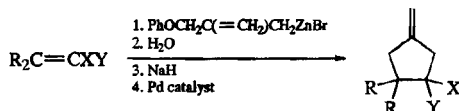
7487 (1989); 112 9022 (1990); 113 7350, 7363
(both intramolecular), 9007 (1991); 114 7375,
7903 (1992); 116 1359 (1994); 117 3284 (1995)
Organomet 1 1543 (1982)
TL 27 1445, 4137 (1986); 28 4547 (1987); 30 1803,
2541 (1989); 34 5765 (1993); 36 6235 (1995)
(intramolecular)
Angew Int 25 1 (1986) (review)
SL 667 (1990)
JOC 57 686 (1992) (intramolecular); 58 4298 (1993)

$\text{MsOCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{SiMe}_3$, cat $\text{Ni}[\text{P}(\text{OEt})_3]_4$

CC 1201 (1986)

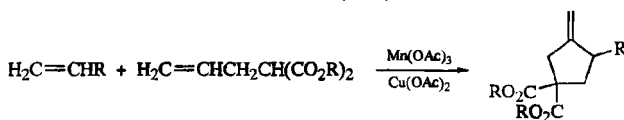


JCS Perkin I 3211 (1992)
SL 27 (1995)

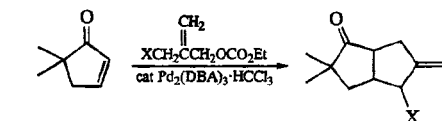


X, Y = CO_2R , CO_2R ; CO_2R , CN; CN, CN

TL 33 475 (1992)



SL 859 (1991)



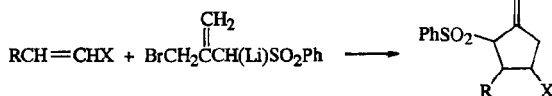
X

ArSO_2

TL 25 5183 (1984); 28 6053 (1987); 30 375 (1989)
(chiral)

CN

TL 25 5183 (1984)



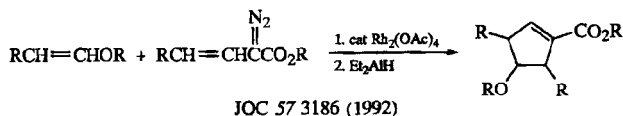
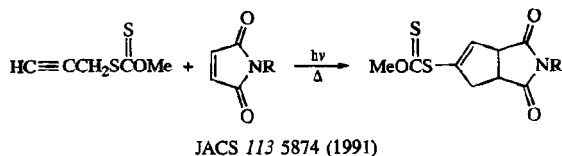
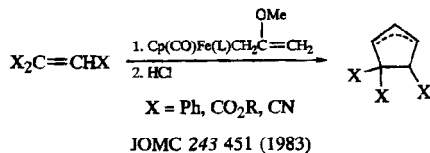
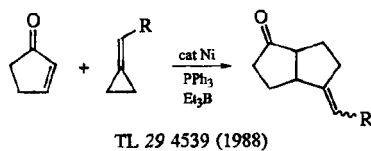
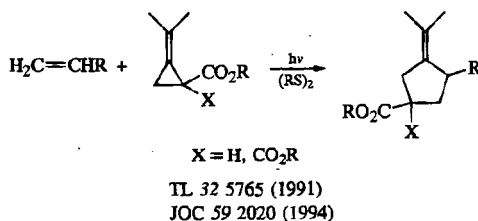
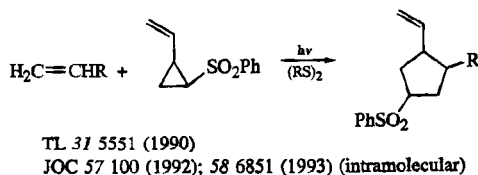
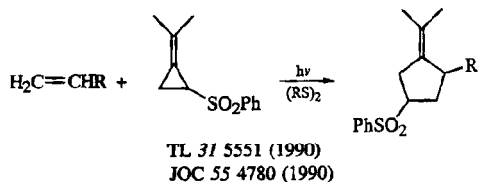
X

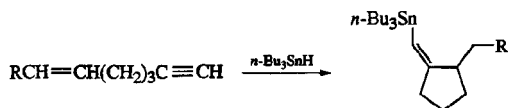
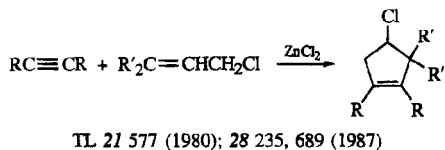
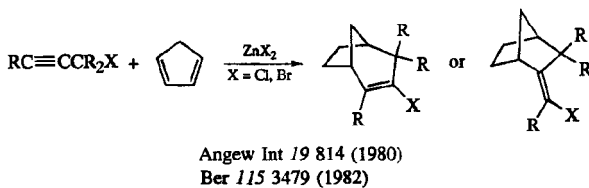
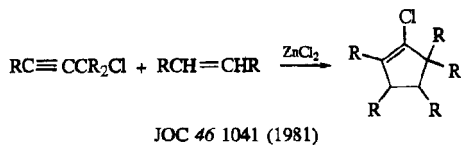
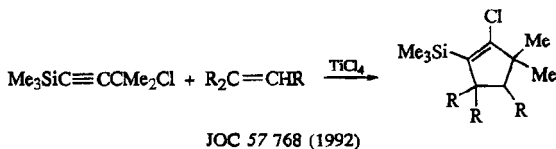
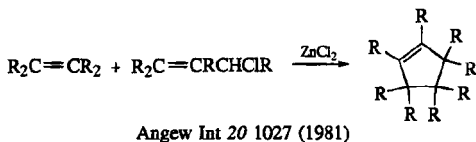
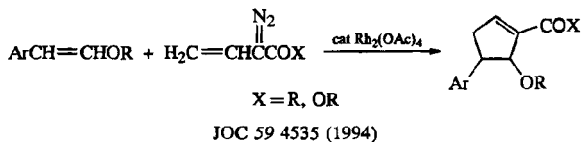
CO_2R

TL 31 3653 (1990)

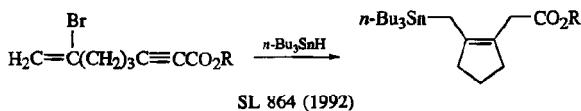
NO_2

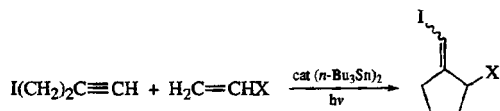
JOC 58 6716 (1993)





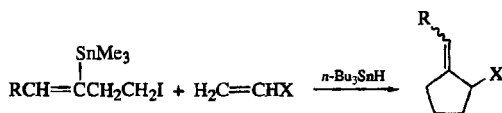
See page 413, Section 2.3.





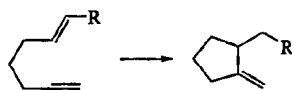
$\text{X} = \text{CHO}, \text{COR}, \text{CO}_2\text{R}, \text{CN}, \text{SO}_2\text{Ph}$

JACS 109 6558 (1987)

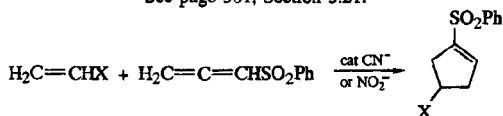


$\text{X} = \text{COR}, \text{CO}_2\text{R}, \text{CN}, \text{SO}_2\text{R}$

TL 30 2501 (1989)

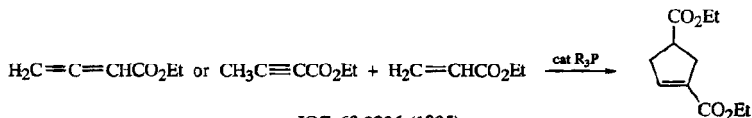


See page 501, Section 3.21.

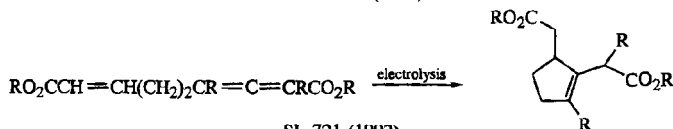


$\text{X} = \text{COR}, \text{CN}$

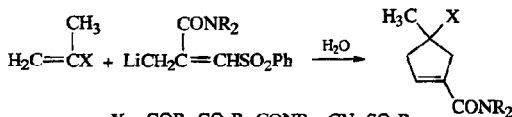
JACS 110 1617 (1988)



JOC 60 2906 (1995)



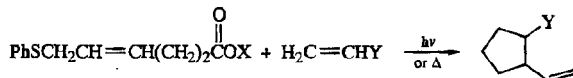
SL 721 (1992)

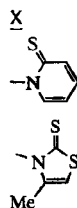


$\text{X} = \text{COR}, \text{CO}_2\text{R}, \text{CONR}_2, \text{CN}, \text{SO}_2\text{R}$

TL 27 5911 (1986)

JOC 54 1647 (1989)

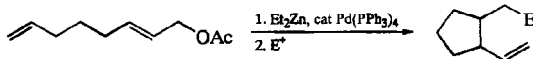


YCHO, COR, CO₂R, CN

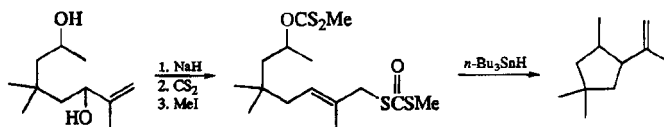
TL 31 4203 (1990)

CN

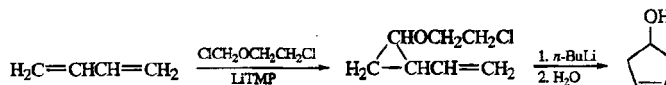
TL 31 6085 (1990)

 $E^+ = \text{NH}_4\text{Cl}, \text{I}_2, \text{CuCN} \cdot 2\text{LiCl} / \text{TsCN} \text{ (E = CN)}$

TL 35 7939 (1994)

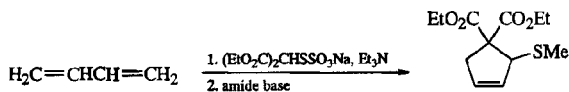


TL 28 5973 (1987)

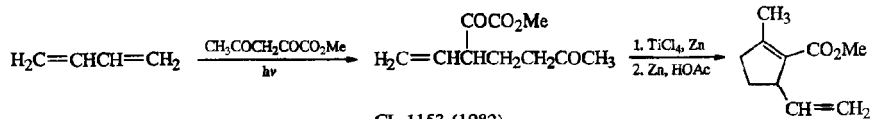


JOC 45 1340 (1980)

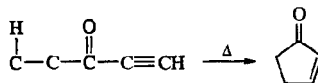
JACS 103 2443 (1981)



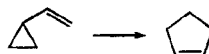
JACS 110 5932 (1988)



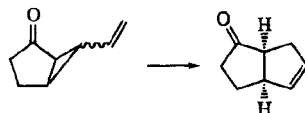
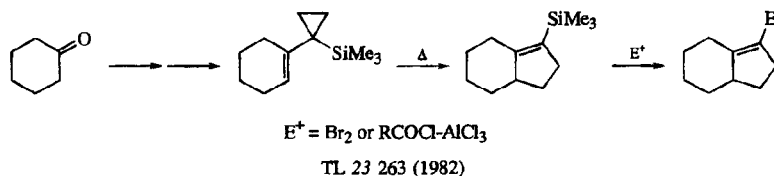
CL 1153 (1982)



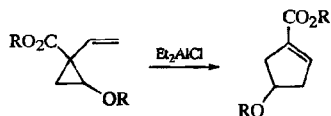
See page 410, Section 2.1.



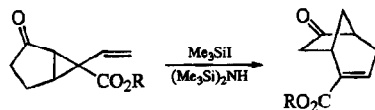
- Δ Russ Chem Rev 45 469 (1976) (review)
 Org Rxs 33 247 (1985) (review)
 JOC 52 4641 (1987); 59 7401 (1994)
 Chem Soc Rev 17 229 (1988) (review)
 JACS 111 6717 (1989); 113 6273, 7432 (1991); 116
 10845 (1994); 117 10672 (1995)
 TL 33 1645 (1992); 35 7905 (1994)
- hv SL 875 (1993) (review)
- cat $[(p\text{-BrC}_6\text{H}_4)_3\text{N}^{+}]\text{SbCl}_6^{-}$ JACS 110 2324 (1988)
- $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ JOMC 117 245 (1976)
- $\text{Mo}(\text{CO})_3(\text{THF})_3$ Ber 100 113 (1967)
 JACS 107 6426 (1985)
- $\text{Fe}_2(\text{CO})_9$ JOMC 160 241 (1978)
- cat $[\text{RhCl}(\text{CO})_2]_2$ CC 1248 (1971)
- cat $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} - \text{Na}_2\text{CO}_3 - \text{H}_2$ Tetr 19 715 (1963)
- cat $\text{Ni}(\text{COD})_2 - \text{R}_3\text{P}$ CL 927 (1979); 2329 (1992) (chiral)
 TL 35 153 (1994)
- cat $\text{Pd}(\text{PPh}_3)_4$ TL 23 2871 (1982); 35 153 (1994)
 Israel J Chem 24 149 (1984)
 CL 2329 (1992)
- cat Cu or CuCl JACS 103 5917 (1981)
 JOC 47 5326 (1982)



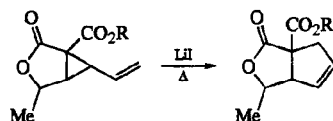
- Δ JOC 40 2265 (1975); 45 5020 (1980)
 TL 27 2885 (1986); 29 611, 3283 (1988)
 JACS 111 6691 (1989)
- cat $\text{Rh}(\text{acac})(\text{C}_2\text{H}_4)_2$ JOC 45 5020 (1980)



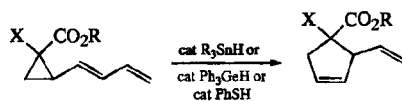
JOC 57 3186 (1992)



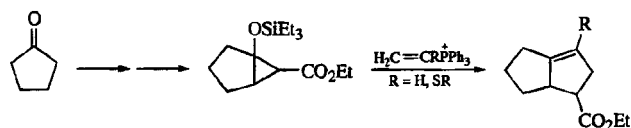
JACS 111 6691 (1989)



TL 32 4591 (1991)

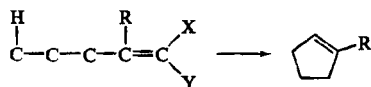
X = CO₂R, SO₂R

TL 29 1543 (1988)



JACS 107 734 (1985)

JOC 52 1, 4139 (1987)



X, Y

H, Cl

H, [†]Ph

H, OTf

Br, Br

I, I

Reagent

LiN(SiMe₃)₂Et₃N or KO-*t*-BuKO-*t*-BuSmI₂SmI₂

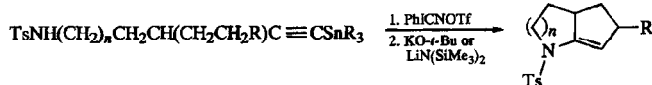
JOC 60 6571 (1995)

JACS 110 6565 (1988)

TL 36 8843 (1995)

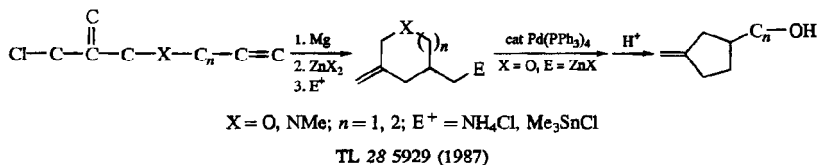
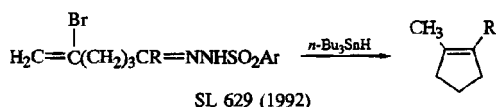
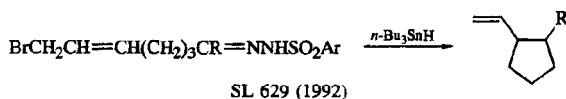
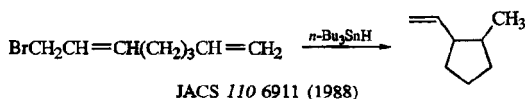
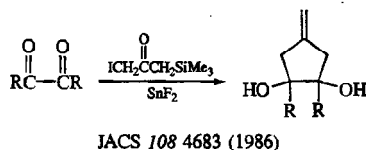
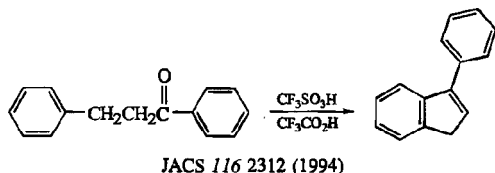
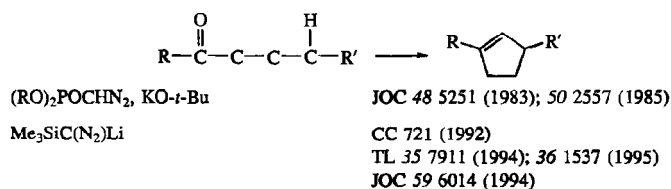
TL 35 7253 (1994)

TL 35 7253 (1994)

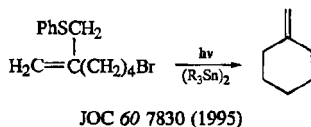


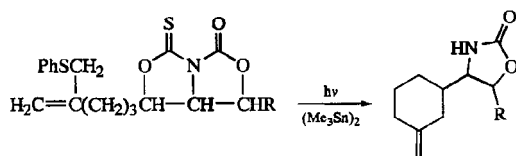
n = 1-3

JACS 117 7544 (1995)

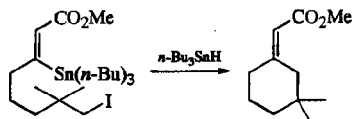


4. Six-Membered Rings

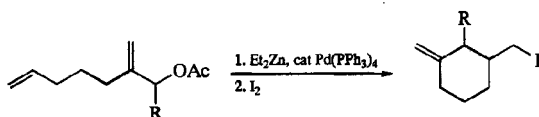




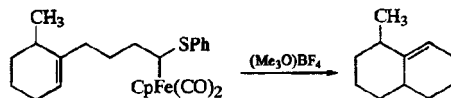
JOC 59 4230 (1994); 60 7830 (1995)



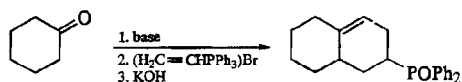
TL 28 2941 (1987)



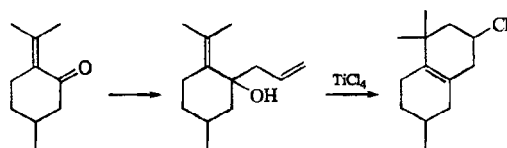
TL 35 7939 (1994)



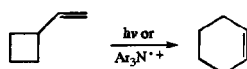
TL 29 4921 (1988)



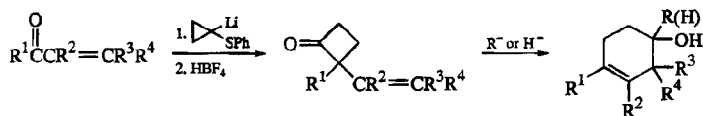
JACS 107 1424 (1985)



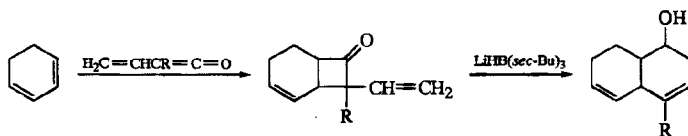
TL 28 2583 (1987)



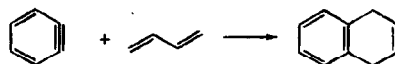
J Phys Org Chem 2 57 (1989) (review)



Tetr 37 3943 (1981)



Tetr 37 3943 (1981)

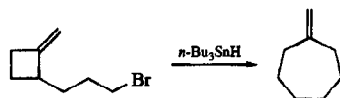


Ann 672 55 (1964)

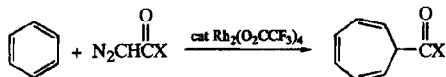
Chem Rev 70 471 (1970) (review)

JOC 38 522 (1973); 40 1355 (1975); 43 2473 (1978)

5. Seven-Membered Rings



TL 36 8539 (1995)



X

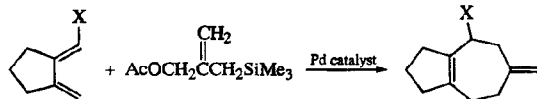
R

OR

CC 491 (1985)

CC 765 (1980)

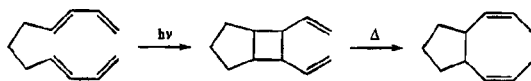
JOC 46 873 (1981)

X = CO₂R, SO₂Ph

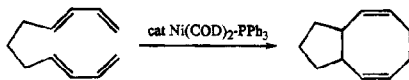
JACS 109 3483 (1987); 113 9007 (1991)

Angew Int 28 213 (1989) (on pyrones)

6. Eight-Membered Rings



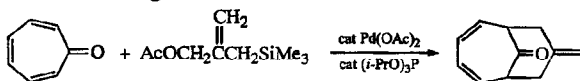
JACS 109 2523 (1987)



JACS 108 4678 (1986); 110 5904 (1988)

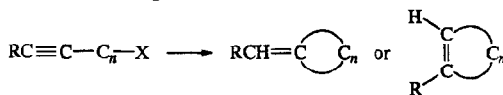
TL 28 2221, 2451 (1987)

7. Nine-Membered Rings

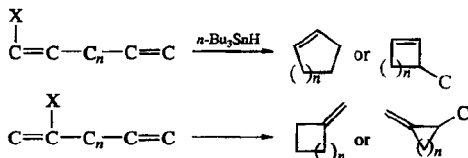


JACS 109 615 (1987); 113 9007 (1991)

8. Various-Membered Rings



See page 413, Section 2.3.



X = Br, I; Ring size = 5-7

JACS 104 2321 (1982); 111 4984 (1984); 112 5601 (1990)

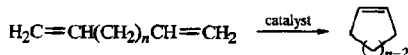
TL 24 1871 (1983); 26 957 (1985) (pyrrolidines); 26 5927 (1985); 27 1355 (cyclic alcohols from enol silanes), 4525 (kinetics, mechanism), 4529 (1986); 29 5789 (1988); 34 2091 (1993)

CC 1445 (1983); 78 (1986) (lactams)

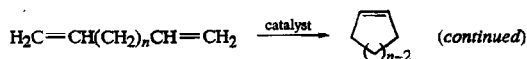
CL 1437 (1984) (3-methylene tetrahydrofurans)

JOC 56 2278, 3097, 3479 (1991); 58 5709 (1993); 59 3636 (1994)

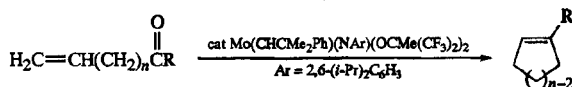
SL 805 (1994)

CatalystMo(CHCMe₂Ph)(NAr)[OCMe(CF₃)₂]₂
[Ar = 2,6-(i-Pr)₂C₆H₃]n
3-6

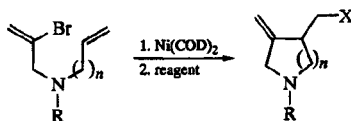
JACS 114 5426 (ethers), 7324 (amines, amides), 10978 (ketones, Si ether) (1992); 115 3800 (1993)

Catalyst

	<u><i>n</i></u>	
		TL 35 691, 6005 (1994); 36 1169 (1995)
		IOC 59 4029 (1994)
$\text{WOCl}_2(\text{OAr})_2$ (Ar = 2,6-dibromophenyl), Et ₄ Pb	3, 4	JACS 117 8992 (1995)
$\text{Re}_2\text{O}_7\text{-SiO}_2\text{-Al}_2\text{O}_3\text{-}n\text{-Bu}_4\text{Sn}$	15	SL 507 (1991)
MeReO ₂ -silica gel-Al ₂ O ₃	4, 5, 12	TL 34 3731 (1993)
$(\text{Cy}_3\text{P})_2\text{RuCl}_2(\text{=CHCH=CPh}_2)$	3-6, 11, 12	JACS 115 9856 (1993); 116 3123 (1994); 117 2108, 5855 (1995)
		TL 35 3191 (1994); 36 1621 (1995)
		SL 1020 (1994)

*n* = 3-5

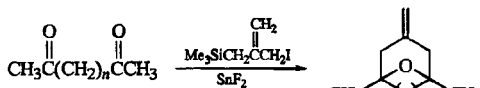
JACS 115 3800 (1993)

*n* = 1, 2Reagent = CO, MeOH (X = CO₂Me); Me₃SiCN (X = CN); NaBH₄ or Et₃SiH (X = H); O₂ (X = OH)

JACS 116 12133 (1994)

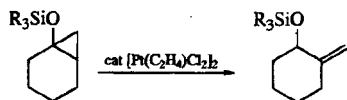
*n* = 1, 2

SL 629 (1992)

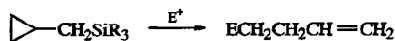
*n* = 2, 3

JACS 109 6877 (1987)

10. MISCELLANEOUS REACTIONS



JACS 114 1520 (1992)



E^+

H^+

Syn 69 (1992)

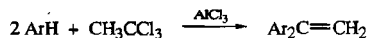
TL 36 7221 (1995)

BBr_3

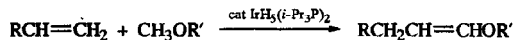
JOC 55 1409 (1990)

SnCl_4

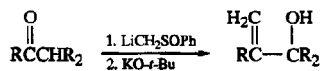
Organomet '6 212 (1987)



SL 925 (1991)

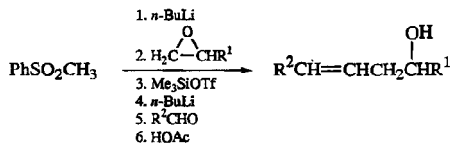


TL 28 3249 (1987)

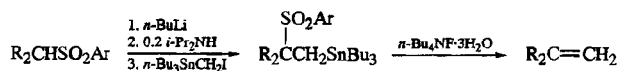


Syn 640 (1980)

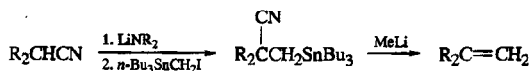
Ber 113 819, 831, 845, 856 (1980)



TL 31 2631 (1990)



JOC 50 3622 (1985)



JOC 50 3625 (1985)

XE⁺

CHO

RCHO

See page 1546, Section 23.

COR

RCHO

See page 1546, Section 23.

 $H_2C=CHCOR$ (1,4-addition)

See page 1546, Section 23.

 CO_2R RCHO, R_2CO

See page 1724, Section 2.

CN

RCHO, R_2CO

See page 1801, Section 6.

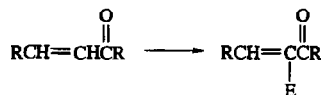
 $H_2C=CHCN$ (1,4-addition)

See page 1801, Section 6.

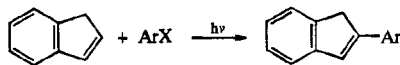
 SO_2Ar

RCHO

See page 1176, Section 2.2.



See page 1546, Section 23.



Ar = furan, thiophene

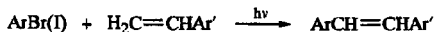
X

Br, I

Heterocycles 29 1331 (1989)

 NO_2

TL 35 633 (1994)



Ar = furan, thiophene

JOC 55 4019 (1990)

ALKYNES

GENERAL REFERENCES

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- Org Rxs 5 1 (1949)
- R. A. Raphael, "Acetylenic Compounds in Organic Synthesis," Butterworths Scientific Publications, London (1955)
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- "Chemistry of Acetylenes," Ed. H. G. Vishe, Marcel Dekker, New York (1969)
- L. Brandsma, "Preparative Acetylenic Chemistry," Elsevier, Amsterdam (1971); Second Edition (1988)
- Syn 235 (1972) (cycloalkynes)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/2a, G. Thieme, Stuttgart (1977)
- "The Chemistry of the Carbon-Carbon Triple Bond," Parts 1 and 2, Ed. S. Patai, J. Wiley, New York (1978)
- J Chem Res (S) 106 (1978); 190 (1979); 270 (1981)
- L. Brandsma and H. D. Verkruijsse, "Synthesis of Acetylenes, Allenes and Cumulenes," Elsevier, New York (1981)
- H. Meier, "Advances in Strain in Organic Chemistry," Ed. B. Halton, JAI Press, Greenwich, CT (1991), Vol 1

1. ISOMERIZATION



n-BuLi/H₂O

Tetr 28 5385 (1972)

t-BuLi/H₂O

TL 36 7607 (1995)



Review: Org Rxs 5 1 (1949)

NaNH₂

BSCF [4] 35 481 (1924)

Ann Chim [10] 3 191, 325 (1925)

JOC 34 222 (1969)

n-BuNHNa

Can J Chem 61 1073 (1983)

K, H₂N(CH₂)₃NH₂

JOC 49 2494 (1984)

K, H₂N(CH₂)₃NH₂, NH₃

JOC 49 2494 (1984)

Na(K)NH₂, H₂N(CH₂)₃NH₂

Rec Trav Chim 96 160 (1977)

LiNHCH₂CH₂NH₂, KO-*t*-Bu

Can J Chem 62 1333 (1984)

JACS 116 8116 (1994)

NaNHCH₂CH₂NH₂

JOC 45 734 (1980)

Can J Chem 60 1238 (1982); 61 1073 (1983)

LiNH(CH₂)₃NH₂, KO-*t*-Bu

Can J Chem 62 1333 (1984)

JOC 52 1835 (1987); 57 1777 (1992)

TL 31 5843 (1990)

Org Syn Coll Vol 8 146 (1993)

NaNH(CH₂)₃NH₂

Can J Chem 58 2567 (1980)

KNH(CH₂)₃NH₂

JACS 97 891 (1975); 109 2138 (1987)

TL 2565 (1976); 411 (1977); 22 4171 (1981); 28 3857 (1987)

CC 959 (1976); 318 (1977)

JOC 55 5433 (1990); 56 6156 (1991); 57 2566 (1992); 58 6779 (1993)

SL 407 (1995)

KNH(CH₂)₃NH₂, NH₃

TL 28 2409 (1987)

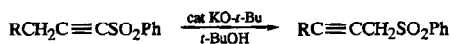


$\text{LiNH}(\text{CH}_2)_3\text{NH}_2$

Can J Chem 61 1073 (1983)

$\text{NaNH}(\text{CH}_2)_3\text{NH}_2$

Can J Chem 58 2567 (1980)



SL 825 (1992)



KOH, EtOH

Org Rxs 5 1 (1949) (review)

JACS 73 1273 (1951)

Quart Rev 24 585 (1970)

KOEt, EtOH

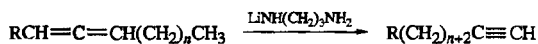
BSCF 805 (1962)

KO-*i*-Bu, DMSO

TL 31 5843 (1990)

NaNH_2 , DMSO

Tetr 26 2127 (1970)



IOC 52 1835 (1987)

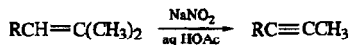
JACS 113 1386 (1991)

2. ELIMINATION REACTIONS

Reviews:

Angew Int 4 49 (1965)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 6, Part 5.1, p 949

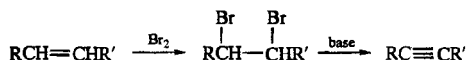


TL 27 267 (1986); 28 4921 (1987); 33 4931 (1992)

JOC 51 2687 (1986)



JOC 32 105 (1967)



Base

KF-alumina (R = R' = Ph)

BCSJ 56 1885 (1983)

NaOH, (n-Bu₄N)HSO₄

TL 4723 (1976)

Org Syn Coll Vol 6 954 (1988)

NaOH or KOH, HO(CH₂CH₂O)_nH

JOC 47 2493 (1982)

KOH, ROH

Org Syn 27 76 (1947)

Org Syn Coll Vol 3 350 (1955)

Ber 89 1786 (1956)

JACS 85 3492 (1963)

J Chem Res (S) 270 (1981)

JOC 54 3224 (1989)

KOH, phase transfer

Tetr 37 1653 (1981)

KO-t-Bu

Helv 54 2060 (1971)

JOC 51 1088 (1986); 58 7498 (1993)

JACS 109 1868 (1987)

TL 28 6359 (1987)

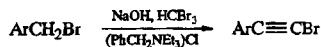
KO-*t*-Bu, 18-crown-6Ann 1 (1980)
TL 34 3103 (1993)Na, NH₃JACS 56 2064, 2120 (1934)
Org Rxs 5 1 (1949)
Rec Trav Chim 85 123 (1960)
Org Syn Coll Vol 4 763 (1963)
TL 41 (1970)
J Chem Res (S) 106 (1978)NaNH₂, NH₃

JOC 58 1900 (1993)

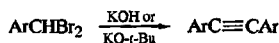
NaNH₂, DMSOTetr 26 2127 (1970)
JOC 53 3148 (1988)

DBU

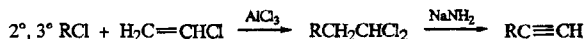
TL 33 3371 (1992)



CC 563 (1979)



JOC USSR 15 579 (1979)

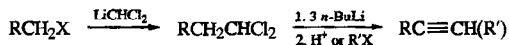


Rec Trav Chim 84 31 (1965)

L. Brandsma, "Preparative Acetylenic Chemistry," Elsevier, Amsterdam (1971), p 189

J Chem Res (S) 106 (1978)

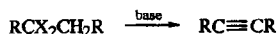
JACS 110 5986 (1988)



Syn 502 (1979)



JOC 59 1213 (1994)



X = Cl, Br

Review: Angew 72 391 (1960)

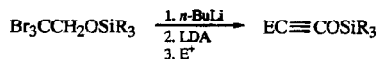
Base

KOH

BSCF 35 357 (1924)
Bull Soc Chim Belg 34 427 (1925)
Ann Chim (10) 16 421 (1931)
JACS 64 543 (1942)
J Chem Res (S) 270 (1981)KO-*t*-Bu, THF

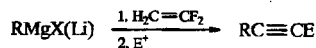
JACS 110 462 (1988)

KO- <i>t</i> -Bu, DMSO	JACS 111 6717 (1989)
KO- <i>t</i> -Bu, 18-crown-6	Ann 1 (1980)
NaNH ₂ , mineral oil	JACS 56 1207 (1934)
NaNH ₂ , NH ₃	Org Rxs 5 1 (1949) Rec Trav Chim 84 31 (1965) J Chem Res (S) 106 (1978) JACS 106 5312 (1984)
NaNH ₂ , DMSO	Tetr 25 4249 (1969)
<i>n</i> -BuLi	Syn 502 (1979)



$\text{E}^+ = \text{EtOH}, \text{MeI}, \text{Me}_3\text{SiCl}$

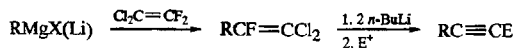
TL 29 4917 (1988)



$\text{R} = 1^\circ, 2^\circ, 3^\circ \text{ alkyl; allylic; aryl; vinylic}$

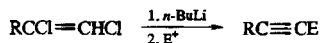
$\text{E}^+ = \text{H}_2\text{O}, n\text{-BuBr}, \text{CH}_3\text{CHO}, \text{Me}_3\text{SiCl}$

TL 23 4325 (1982)



$\text{E}^+ = \text{H}_2\text{O}, \text{CO}_2$

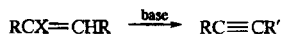
JOC 41 1487 (1976)



$\text{E}^+ = \text{H}_2\text{O}, \text{RX}$

Org Syn Coll Vol 7 241 (1990)

JOC 60 7690 (1995)



Review: Angew 72 391 (1960)

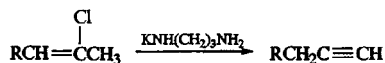
X

Base

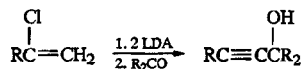
Cl

NaOH, (<i>n</i> -Bu ₄ N)HSO ₄	TL 4723 (1976); 33 4041 (1992)
KOH	JACS 63 1175 (1941)
NaOMe, MeOH	JOC 26 2619 (1961)
NaOEt	Ann 308 264 (1899)
KO- <i>t</i> -Bu	JCS Perkin II 795 (1982)

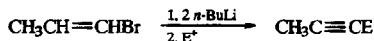
<u>X</u>	<u>Base</u>	
	NaNH ₂ , toluene	JOC 34 222 (1969)
	LDA	TL 31 6753 (1990)
		SL 279 (1991)
	<i>n</i> -Bu ₄ NF	JOC 53 2655 (1988)
Cl, Br	KF or Et ₄ NF	JCS Perkin I 340 (1974)
	(PhCH ₂ NMe ₃)OH	BSCF II 125 (1976)
	KO- <i>t</i> -Bu, 18-crown-6	Ann 1 (1980)
	NaNH ₂ , mineral oil	JACS 56 1207 (1934)
	NaNH ₂ , NH ₃	Ann Chim [10] 3 325 (1925); 7 785 (1962)
		JACS 56 2064, 2120 (1934)
		Org Syn Coll Vol I 185 (1941); 8 161 (1993)
		Org Rxs 5 1 (1949)
		Org Syn 65 68 (1987)
Br	K ₂ CO ₃ , EtCOMe (R = CH ₂ OR)	JOC 47 2484 (1982)
	NaOH, EtOH	JACS 76 4558 (1954)
		J Chem Res (S) 270 (1981)
	KOH	Org Syn Coll Vol I 438 (1941)
	KO- <i>t</i> -Bu	Angew Int 4 953 (1965)
	KO- <i>t</i> -Bu, <i>t</i> -BuOH	Ann 707 66 (1967)
	DBU	JOC 47 2484 (1982)
	NaNH ₂ , DMSO	Tetr 26 2127 (1970)
	NaH or NaNH ₂ , HMPA	BSCF 1293 (1966)
	LDA	JOC 52 5622 (1987)
		JACS 115 3846 (1993)
		TL 34 5253 (1993)
I	NaOH, (<i>n</i> -Bu ₄ N)HSO ₄	TL 34 2931 (1993)
	KOH, EtOH	JOC 34 3502 (1969)
	KO- <i>t</i> -Bu	JOC 47 2251 (1982)
	KO- <i>t</i> -Bu, <i>t</i> -BuOH	JOC 34 3502 (1969)
	DBU	JOC 47 2251 (1982)
	LiNH ₂ , NH ₃	TL 30 7083 (1989)
	LDA	TL 30 7083 (1989)
OCON(<i>i</i> -Pr) ₂	<i>n</i> -BuLi	SL 611 (1991)
OTf	2,6-(<i>t</i> -Bu) ₂ C ₆ H ₃ OK	CC 459 (1981)
	LDA	CC 459 (1981)
		TL 34 5257 (1993)
O ₃ SR, O ⁺ PAr ₃ , OPO(OR) ₂	—	Angew Int 8 429 (1969)
SR	NaNH ₂ , NH ₃	TL 33 4229 (1992)



TL 28 4547 (1987)



TL 28 5793 (1987)

 $\text{E}^+ = \text{RCHO}, \text{R}_2\text{CO} (\text{CeCl}_3), \text{RCOCl} [\text{ZnCl}_2, \text{cat Pd}(\text{PPh}_3)_4], \text{RCONMeOMe}$

JOC 60 3550 (1995)

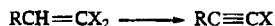


JOC 58 5802 (1993)



Ann 279 319, 324, 337 (1894)

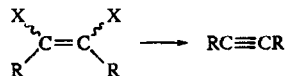
Angew Int 4 49 (1965) (review)

XReagent(s)

Cl

KOH, Aliquat 336
LiNEt₂TL 33 683 (1992)
Syn 458 (1975)

Br

NaOH, PEG-400
KOH
(PhCH₂NMe₃)OH
DBU, DMSO
NaN(SiMe₃)₂JOC 51 4354 (1986)
JOC 58 5918 (1993)
Ann 2061 (1980)
TL 35 4777 (1994)
TL 33 5355 (1992); 35 3529
(1994)*n*-Bu₄NFJACS 111 5330 (1989)
JOC 56 2225 (1991)
SL 54 (1994)XReagent

Cl

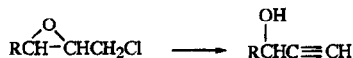
n-BuLi

Org Syn 64 73 (1985)

Br

Zn or Zn(Hg)

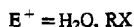
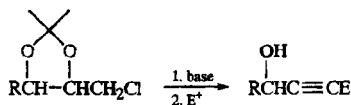
TL 35 6243 (1994)

*n*-BuLiCC 1344 (1989)
SL 451 (1990); 279 (1991)
JACS 115 11393 (1993)LiNH₂

TL 31 4495 (1990)

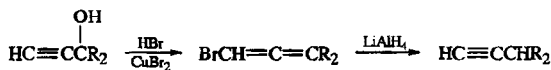
LDA

TL 31 4495 (1990)



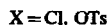
TL 29 2737 (1988); 30 5455 (1989); 34 1191 (1993)

SL 453, 591 (1990); 119 (1994)

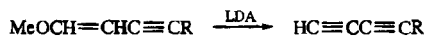


JOC 33 3655 (1968)

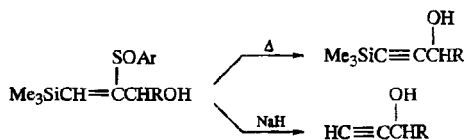
J Chem Res (S) 106 (1978)



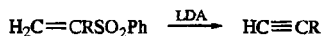
TL 33 4703 (1992)



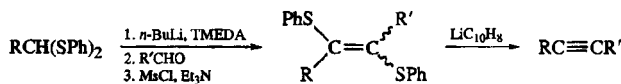
TL 31 6815 (1990)



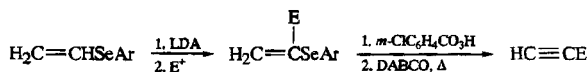
TL 34 6587 (1993)



SL 863 (1993)



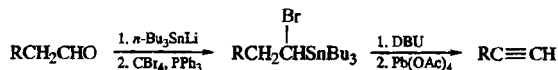
SL 628 (1995)



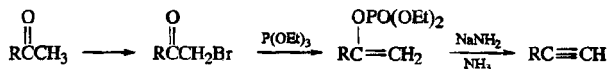
JACS 102 5967 (1980)



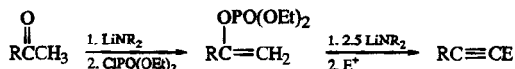
JACS 112 3717 (1990)



TL 23 4607 (1982)



JCS 3712 (1963)

 $\text{E}^+ = \text{H}_2\text{O}, \text{CH}_2\text{O}, \text{ClCO}_2\text{Me}, \text{Me}_3\text{SiCl}$

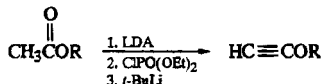
JOC 45 2526 (1980); 52 398, 4885 (1987); 56 5138 (1991)

Org Syn 64 44 (1985)

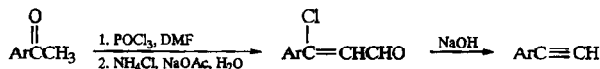
JACS 107 2568 (1985); 108 3835 (1986); 111 3336 (1989); 116 7588 (1994)

TL 28 5793 (1987); 34 5257 (1993); 36 5379 (1995)

Org Syn Coll Vol 7 63 (1990)



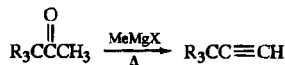
JOC 59 7523 (1994)



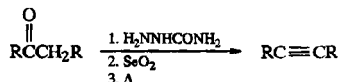
Ber 98 3554 (1965)

Org Prep Proc Int 7 79 (1975)

JOC 57 7248 (1992)



JCS Perkin I 1079 (1982)



Angew Int 9 464 (1970)

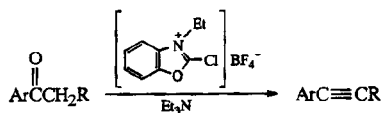
CC 1059 (1971)

Tetr 28 187 (1972)

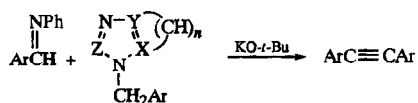
Ber 113 2398 (1980)

JACS 110 462 (1988); 113 9258 (1991)

TL 29 2813 (1988); 35 8353 (1994)



CL 481 (1979)

 $\text{X}=\text{Y}=\text{C}, \text{Z}=\text{N} \text{ or } \text{CH}, n=4$ $\text{X}=\text{N}, \text{Y}=\text{Z}=\text{CH}, n=0$

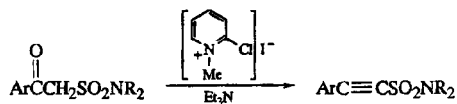
TL 33 6405 (1992)

 $\text{TiF}_2\text{O}, i\text{-Pr}_2\text{NEt}$

SL 825 (1992)

 $\text{ClPO}(\text{OEt})_2, \text{Et}_3\text{N}/\text{KO}-t\text{-Bu}$

TL 34 4477 (1993)



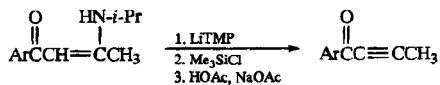
TL 31 3875 (1990)

 $\text{Et}_2\text{NCF}_2\text{CHF}\text{X} (\text{X}=\text{Cl}, \text{CF}_3; \text{R}'=\text{R} \text{ or } \text{OR})$

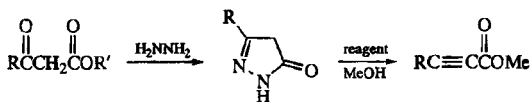
CL 1327 (1980)

 $\text{H}_2\text{NNH}_2/\text{Br}_2/\text{NaOH}/\text{HCl} (\text{R}'=\text{OR})$

Syn 72 (1981)



TL 32 7091 (1991)



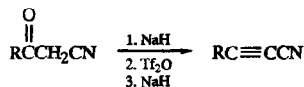
ReagentTi(NO₃)₃

Angew Int 11 48 (1972)

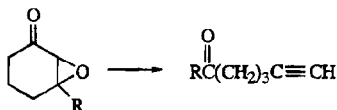
Org Syn Coll Vol 6 791 (1988)

Pb(OAc)₄

Syn 1100 (1982)



JACS 106 462 (1984)

TsNHNH₂

Helv 50 708 (1967); 54 2896 (1971)

TL 3739, 3943 (1967)

SL 787 (1991)

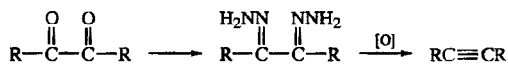
JOC 56 1393 (1991); 57 50 (1992); 58 1900 (1993);

60 2714 (1995)



Helv 55 1276 (1972)

Org Syn Coll Vol 6 679 (1988)

Oxidant

HgO

JACS 74 3636, 3643 (1952)

Helv 35 1598 (1952)

Org Syn Coll Vol 4 377 (1963)

Pb(OAc)₄

TL 4511 (1968)

AgO₂CCF₃, Et₃N

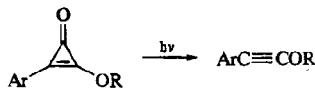
JOC 23 665 (1958)

(EtO)₃P, Δ

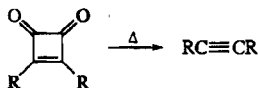
JOC 29 2243 (1964)

O₂, CuCl, py

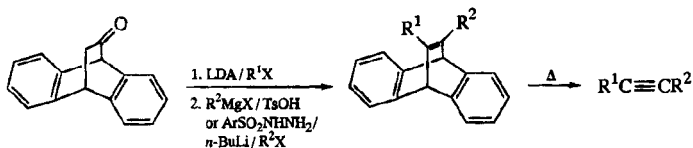
TL 4573 (1973)



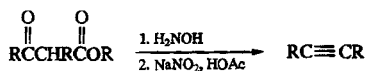
JOC 59 4319 (1994)



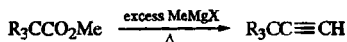
JACS 113 6943 (1991) (polyynes)



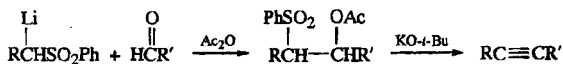
CL 1241 (1981)



TL 32 5321 (1991); 36 5737 (1995)

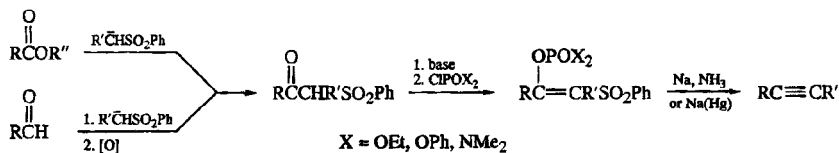


JCS Perkin I 1079 (1982)



JACS 106 3670 (1984)

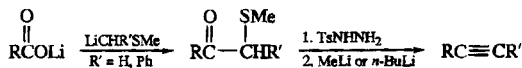
JOC 51 3830 (1986)



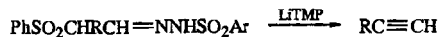
JACS 100 4852 (1978)

TL 2625 (1978)

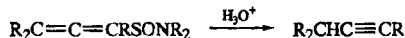
JCS Perkin I 2429 (1979)



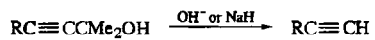
JOC 43 4366 (1978)



JACS 115 3846 (1993)



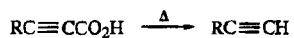
TL 30 4965 (1989)



JOC 44 1233 (1979); 48 5135 (1983); 50 1763 (1985); 57 6998 (1992); 59 5818 (1994)

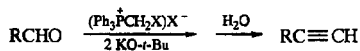
Acta Chem Scand B 42 448 (1988)

SL 299 (1994)



Helv 54 2060 (1971)

3. WITTIG AND RELATED APPROACHES



R = aryl > alkyl

X

Cl

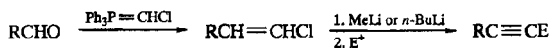
CC 446 (1978)

SL 833 (1995)

Br

TL 21 4021 (1980); 27 5853 (1986)

SL 833 (1995)



E⁺

H₂O

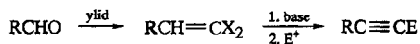
JACS 91 4318 (1969)

TL 1495 (1973)

Tetr 44 1673 (1988)

ClCO₂Me

TL 28 5473 (1987)



E⁺ = H₂O, RX, RCHO, R₂CO, RCOCl, CO₂, ClCO₂Me, ClCONR₂, ROCO₂R, R₃SiCl, I₂

(Me₂N)₃P=CCl₂ / *n*-BuLi / E⁺

Gazz Chim Ital 110 195 (1980)

BSCF II 189 (1983)

Ph₃P, CBr₄, (Zn) / *n*-BuLi or Li(Hg) / E⁺

TL 3769 (1972); 27 3059 (1986); 28 1143, 2099

(1987); 30 4845 (1989); 31 3957 (1990); 32 4115

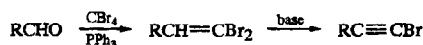
(1991); 36 8275 (1995)

Gazz Chim Ital 110 195 (1980)

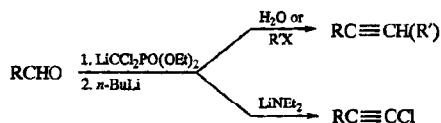
Tetr 37 3873 (1981)

Ber 115 828 (1982)

- BCSJ 55 2221 (1982)
 JACS 106 1501 (1984); 108 2776 (1986); 111 8037 (1989); 112 9292 (1990); 113 1355, 3873, 5337, 6958 (1991); 114 369, 7360, 9369, 10653 (1992); 115 11393 (1993); 116 7588 (1994); 117 1908 (1995)
 JOC 52 5243 (1987); 54 500 (1989); 56 1083 (1991); 57 5060 (1992); 58 600, 3912, 4662, 5690, 6833 (1993)
 SL 463, 863 (1993); 607 (1994); 193 (1995)
- Ph_3P , $\text{CBr}_4/\text{Mg}/\text{H}_2\text{O}$ TL 30 3655 (1989)
- Ph_3P , CBr_4 , $\text{Zn}/\text{MeMgBr}/\text{E}^+$ TL 36 2733 (1995)



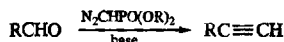
See page 569, Section 2.



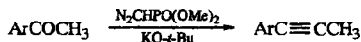
Syn 458 (1975)
 JOC 42 28 (1977)
 Gazz Chim Ital 110 195 (1980)
 TL 27 87 (1986)
 JACS 113 5378 (1991)



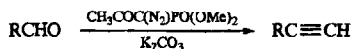
CL 935 (1980)



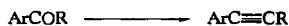
JOC 44 4997 (1979); 47 1837 (1982); 57 5071 (1992); 58 832 (1993)
 TL 30 1521 (1989); 32 2343 (1991); 33 3715 (1992); 36 8299, 8765 (1995)
 JACS 112 5583 (1990)
 SL 231 (1994)



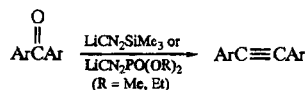
JOC 44 4997 (1979); 47 1837 (1982)



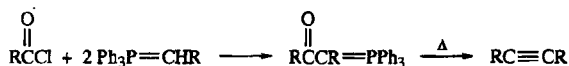
Syn Commun 19 561 (1989)
 TL 36 877 (1995)



SL 107 (1994)



JCS Perkin I 869 (1977)



JCS 3874 (1959); 2333 (1962); 543 (1964)

Proc Chem Soc 302 (1961)

Ber 94 3005 (1961)

Angew Int J 160 (1962)

JOC 30 1015 (1965); 53 5558 (1988); 57 5680 (1992)

BCSJ 44 2231 (1971)

Ann 282 (1977)

TL 22 5283 (1981); 23 343 (1982); 25 1111 (1984); 26 5137 (1985); 34 5621 (1993); 35 139 (1994)

Chem Pharm Bull 32 4402 (1984)

Syn 35, 240, 924 (1984); 159 (1985); 42, 626 (1987)

CC 1140 (1985)

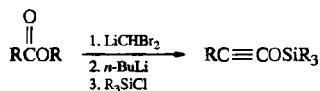
JCS Perkin I 1579 (1987)

J Fluorine Chem 35 513 (1987); 40 15 (1988); 41 363 (1988)

Syn Commun 19 2877 (1989)

SL 211, 212 (1990)

Tetr 48 7609 (1992)



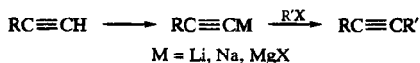
JACS 108 7127 (1986)

4. ALKYLATION, ALKENYLATION AND ARYLATION OF ALKYNES AND ALLENES

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.7, p 271

1. Organolithium, -sodium and -magnesium Compounds

See also page 596, Section 10 and page 599, Section 11.



JACS 58 796 (1936); 60 1882 (1938) (R'X = EtOTs); 114 8921 (1992); 115 2156 (1993) (R' = CF₃)

JOC 2 1 (1937); 24 840 (1959); 51 4158 (1986); 56 2883, 7183 (1991); 58 5964 (1993)

Org Rxs 5 1 (1949) (review)

JCS 893 (1951)

Org Syn Coll Vol 4 117 (1963); 6 273 (1988)

BSCF 2000 (1964); 1525 (1965)

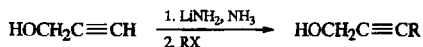
Syn 567 (1972); 441 (1974); 423 (1975)

Syn Commun 3 245 (1973)

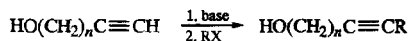
J Chem Res (S) 106 (1978); 190 (1979); 270 (1981) (reviews)

CL 669 (1980)

TL 27 5445 (1986); 31 4609 (1990) (R'OTf); 35 9501 (1994)



Org Syn Coll Vol 8 415 (1993)



Base

LiNH₂, NH₃

Helv 61 2275 (1978)

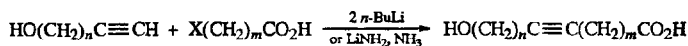
n-BuLi

JACS 110 8117 (1988)

TL 31 7615 (1990)

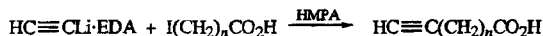
EtMgBr

TL 31 4923 (1990)



$$n = 1, 2; m = 4, 5, 10, 11; \text{X} = \text{Br}, \text{I}$$

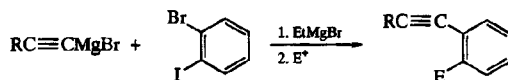
TL 27 573, 2279, 2369 (1986)



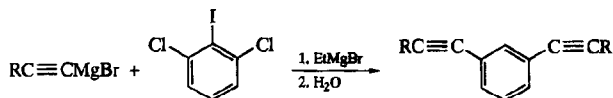
Syn Commun 10 653 (1980)



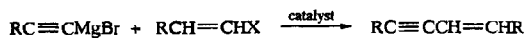
Syn 292 (1979)



JOC 52 4311 (1987)



JOC 52 4311 (1987)



X

Catalyst

halogen

Ni

JOC 49 4733 (1984)

JACS 108 4685 (1986)

Pd

TL 191 (1978)

Tetr 37 2617 (1981)

JACS 107 1028 (1985)

SL 665 (1994)

OCON(*i*-Pr)₂

Ni

SL 435 (1995)



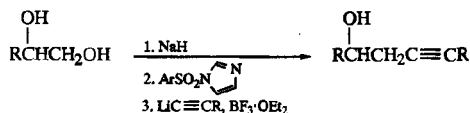
M = Li, MgX

A. W. Johnson, "The Chemistry of Acetylenic Compounds," Vol 1, "Acetylenic Alcohols," Edward Arnold and Co., London (1946) (review)

JOC 22 1611 (1957)

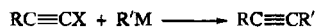
CL 447 (1979); 255 (1980) (asymmetric)

CC 363 (1981) (stereochemistry)



JOC 60 8122 (1995)

For other organometallics, see page 88, Section 2.1 and page 392, Section 22.


X
R'M

SPh

t-BuLi

JOC 54 1836 (1989)

 SO₂Ar

R'Li

JOC 44 3444 (1979); 54 1836 (1989)

R'MgX

JOC 44 3444 (1979); 54 1836 (1989)

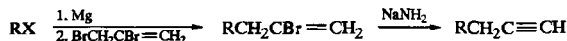

 R' = Me, *i*-Pr

TL 5041 (1968); 2247 (1970); 23 719 (1982); 27 2187 (1986); 29 2819 (1988)

JACS 90 5618 (1968); 92 6314 (1970)



JOC 46 5041 (1981)



BSCF [4] 29 528 (1921)

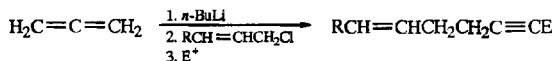
Ann Chim [10] 3 325 (1925)

Org Syn Coll Vol 1 180, 185 (1941)

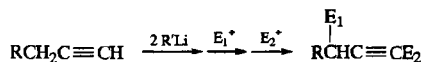


JCS 4244 (1955)

TL 2249 (1970)


 E⁺ = H₂O, (CH₂O)_n

Org Syn Coll Vol 8 226 (1993)


E₁⁺
E₂⁺

 H₂O

 H₂O

JOMC 3 165 (1965)

RX

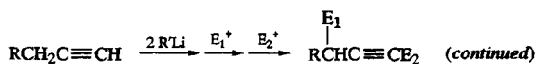
 H₂O

CC 1030 (1974)

JOC 46 5041 (1981) (R = SPh)

Org Syn Coll Vol 6 595 (1988)

SL 415 (1994)

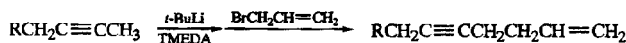


E_1^+	E_2^+	
RX (continued)	H ₂ O, RX, H ₂ CO, I ₂	CC 817 (1975)
	H ₂ O, RX, RCHO, R ₂ CO, R ₃ SiCl	JACS 103 3112 (1981)
		(R = SePh)
	H ₂ O, Me ₂ SO ₄ , RX, H ₂ CO, R ₂ CO	Syn 321 (1976)
	RX, epoxide, H ₂ CO, I ₂	JCS Perkin I 1218 (1979)
RX, epoxide, R ₃ SiCl	H ₂ O	Rec Trav Chim Pays-Bas 99 113 (1980)
Et ₂ SO ₄	Et ₂ SO ₄	JACS 98 8413 (1976)
epoxide	H ₂ O	JOC 58 5452 (1993)
H ₂ CO	H ₂ CO	CC 215 (1979)
		JCS Perkin I 2338 (1980)
RCHO	H ₂ O	SL 679 (1992)
	RCHO	JACS 98 8413 (1976)
R ₂ CO	R ₂ CO	Syn 321 (1976)
		CC 215 (1979)
		JCS Perkin I 2338 (1980)
RCH=NR	H ₂ O	JCS Perkin I 2338 (1980)
R ₃ SiCl	R ₃ SiCl	Tetr 28 5385 (1972)
		JACS 98 8413 (1976)

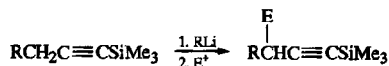
For metallation, see also:


JACS 91 3094 (1969)

Tetr 26 2345 (1970)



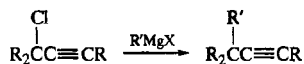
JOC 47 3364 (1982)



E^+	
RX	JACS 108 1359 (1986)
	SL 667 (1990)
RCHO, Ti(O- <i>i</i> -Pr) ₄	SL 864 (1992)



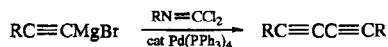
JOC 52 1889 (1987)



JACS 62 1798 (1940); 68 1202 (1946); 86 5244 (1964); 89 6177 (1967)

J Chem Res (S) 106 (1978); 190 (1979)

JOC 58 5452 (1993)



TL 29 5379 (1988)

2. Organoboron Compounds

See also page 596, Section 10.



Reagent

I₂

JACS 95 3080 (1973); 110 1529 (1988)

JOC 39 731 (1974); 46 2311 (1981); 51 162, 4507,

4514 (1986); 52 2919 (1987)

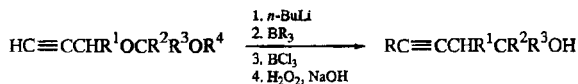
TL 1961 (1975); 29 4181 (1988)

Syn 679 (1977)

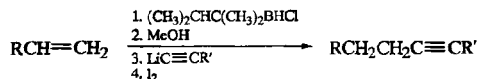
Ber 115 828 (1982)

CH₃SOCl

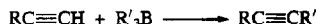
TL 1847 (1973)



TL 36 8209 (1995)



JOC 51 4518, 4521 (1986); 56 1500 (1991) (chiral)

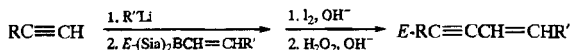


electrolysis

CL 999 (1977); 461 (1980)

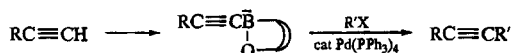
Pb(OAc)₄

CL 413 (1980)



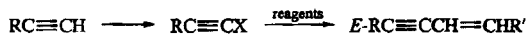
CC 874 (1973)

TL 411 (1977); 27 539 (1986)



R' = aryl, vinylic

TL 36 6847 (1995)



Reagents

E-RCH=CHBR₂, cat Pd(PPh₃)₄, base

TL 3437 (1979); 22 127 (1981); 32 2311 (1991)

Tetr 37 2617 (1981)

JACS 107 972 (1985)

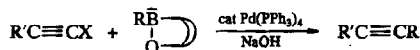
Pure Appl Chem 57 1749 (1985)

E-RCH=CHB(Sia)₂, NaOMe, CuCN

JACS 106 462 (1984)

E-RCH=CHB , NaOMe, CuI

IOC 46 645 (1981)



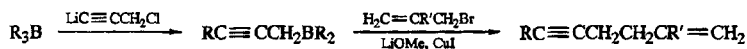
R

Me

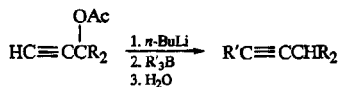
TL 31 5541 (1990)

CH₂Si(CH₃)₃

TL 31 4981 (1990)



CL 1289 (1982)



IOC 42 2650 (1977)

3. Organoaluminum Compounds

See also page 594, Section 8, and page 596, Section 10.



JACS 97 7385 (1975)

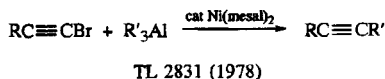
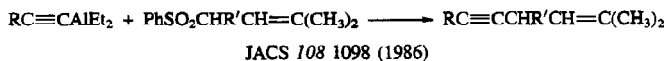


TL 31 5345 (1990)

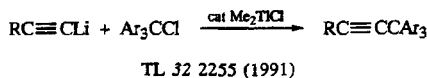


TL 21 2531 (1980); 22 1609 (1981)

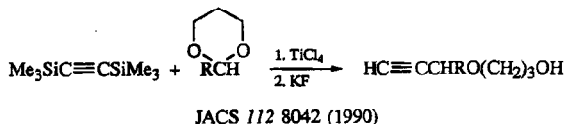
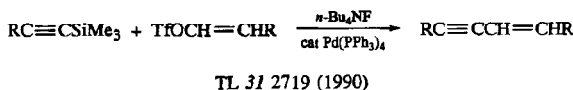
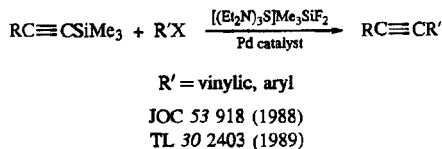
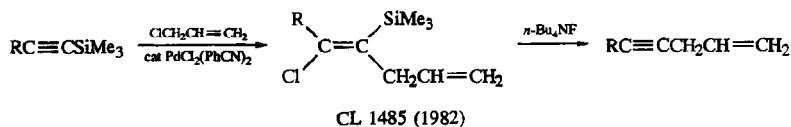
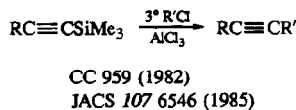
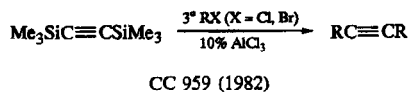
BCSJ 57 108 (1984)

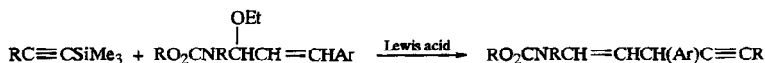


4. Organothallium Compounds

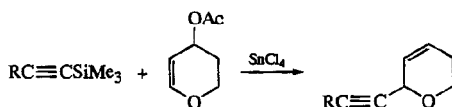


5. Organosilicon Compounds





SL 99 (1991)



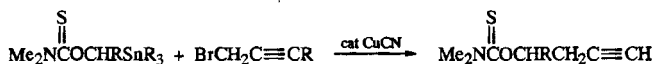
TL 33 7911 (1992)

SL 413 (1993)

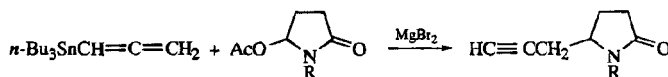


TL 34 2383 (1993)

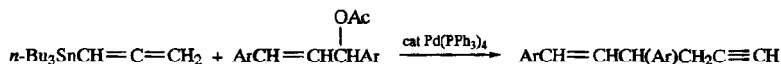
6. Organotin Compounds



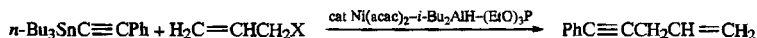
JACS 117 5973 (1995)



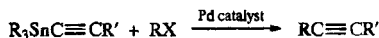
JOC 60 103 (1995)



JOC 48 5302 (1983)



JOC 60 5752 (1995)

RXR_fIROCH₂X (X = Cl, Br), RSCH₂ClH₂C=CHCH₂Cl(Br)

ArX

TL 28 5857 (1987)

TL 33 4885 (1992)

JOC 60 5752 (1995)

Izv Akad Nauk SSSR, Ser Khim 479 (1980)
[CA 93 26019h (1980)]

- JOC USSR 17 18 (1981)
 JOMC 250 551 (1983)
 Proc Acad Sci USSR, Chem Sec 272 333 (1983); 274 39 (1984)
 JOC 54 5856 (1989); 59 5905 (1994)
 SL 502 (1992)
 TL 35 857 (1994)
- heterocyclic halides
 JACS 109 2138 (1987) (thiophene)
- ArOTf
 JACS 109 5478 (1987)
 JOC 57 678 (1992)
 Syn Commun 23 1489 (1993)
- RCH=CHI(Br)
 JACS 109 2138 (1987); 111 4120 (1989) (intramolecular); 112 9330 (1990); 113 9851 (1991) (intramolecular); 115 6991, 7021 (1993)
 TL 29 1509 (1988); 30 2403 (1989); 31 4293, 4329 (intramolecular) (1990); 32 3329 (1991); 34 669 (intramolecular), 3663, 3679 (1993); 35 2081, 6551 (1994)
 SL 157, 651 (intramolecular) (1991); 123 (on polymer), 998 (1994)
 JOC 58 7870 (1993); 59 5393 (1994); 60 3592 (1995)
- $(R_2C=CHI(Ph)OTf)^+$
 JACS 115 11626 (1993)
- RCH=CHOTf
 JACS 106 4630 (1984); 108 3033 (1986); 111 5417 (1989); 113 3873 (1991)
 TL 27 1523 (1986); 29 6043 (1988); 32 6675 (1991)
 JOC 55 5833 (1990); 57 4043 (1992); 60 7821 (1995)
 SL 123 (1994); 871 (1995)

For $RX = RCOCl$, see page 1389, Section 2.6.



TL 27 3479 (1986)



RX

$RCONHCHXCO_2R$ ($X = Cl, Br$)

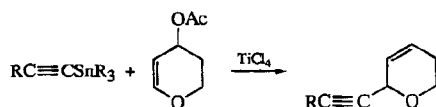
JOC 55 4657 (1990)

$RXCH_2Cl$ ($X = O, S, NR$)

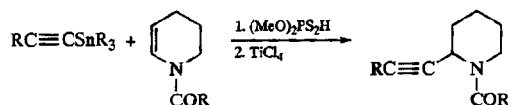
JACS 110 2501 (1988)



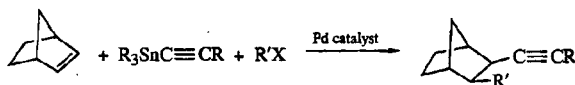
SL 99 (1991)



TL 33 7911 (1992)



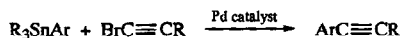
SL 797 (1991)



R' = aryl, vinylic

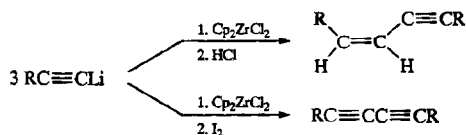
Tetr 45 961 (1989)

BCSJ 66 3522 (1993)

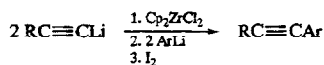


SL 771 (1993)

7. Organozirconium Compounds

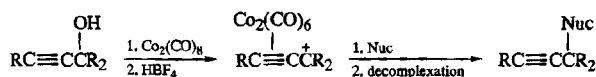


JACS 113 1440 (1991)



JACS 113 1440 (1991)

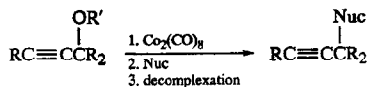
8. Organocobalt Compounds

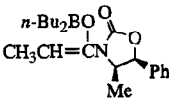


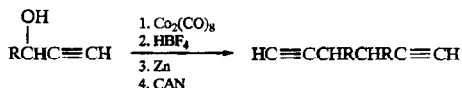
Review: Acct Chem Rev 20 207 (1987)

Nuc

NaBH ₄	JACS 107 4999 (1985)
methoxyarenes	TL 4163 (1977) SL 70 (1992)
indole	SL 529 (1993)
allylic silanes	TL 21 1595 (1980) JACS 108 3128 (1986) (intramolecular); 115 6438 (1993) (phosphite complex) SL 70 (1992)
allylic stannane	SL 70 (1992)
<i>n</i> -Bu ₃ SnCH=C=CH ₂ (alkyne formed)	SL 70 (1992)
enamine	SL 435 (1992)
ketones, enol silanes, enol acetates	JACS 102 2508 (1980)
enol silane	JACS 108 3128 (1986); 115 6438 (1993) (phosphite complex) CC 1353 (1987) TL 30 851 (1989) (intramolecular) SL 70 (1992); 769 (1993) (intramolecular); 713 (1994) (intramolecular); 714 (1995) (intramolecular) Org Syn Coll Vol 8 460 (1993) JOC 60 7496 (1995)
dienyl ketene acetal	JACS 115 6438 (1993) (phosphite complex)
isopropenyl acetate	Syn Commun 10 503 (1980)
β -diketones, β -keto esters	TL 4349 (1978)
See also TL 23 2555 (1982); 26 1269 (1985).	


R'
Nuc

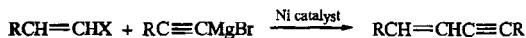
Me	allylic silane, BF ₃ ·OEt ₂ ; enol silane, Lewis acid enol silane	JACS 108 3128 (1986) SL 769 (1993) (intramolecular)
		JACS 109 5749 (1987)
Ac	AlMe ₃ Al(C≡CR) ₃	JOMC 212 115 (1981) TL 24 2239 (1983)



TL 35 363 (1994)

9. Organonickel Compounds

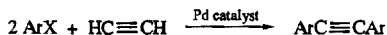
See also page 590, Section 3, and page 592, Section 6.



See page 585, Section 1.

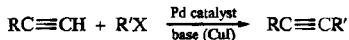
10. Organopalladium Compounds

See also page 589, Section 2; page 590, Section 3; page 591, Section 5; and page 592, Section 6.



TL 4467 (1975)

JACS 116 8152 (1994)



Reviews:

Org Prep Proc Int 27 127 (1995)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 2.4, p 521

R'X

ArX

TL 4467 (1975); 27 1653 (1986); 28 2887, 3857, 4879, 5395, 5981 (1987); 31 4449 (1990); 33 4229, 6431 (1992); 34 6403 (1993); 35 3501, 6113, 6993 (1994); 36 4525, 6017, 6607 (1995)

JOMC 93 253, 259 (1975)

Syn 627 (1980)

JOC 46 2280 (1981); 53 2489 (1988); 54 249, 4453 (1989); 55 63 (1990); 57 3218, 6998 (1992); 58 3018, 6559, 6614, 7368, 7870 (1993); 59 1108, 1294, 1855, 2506, 5818, 6084, 7142, 7164, 7876 (1994); 60 5266, 5814, 7096, 7186 (1995)

JOC USSR 18 308, 1283 (1982)

JACS 107 5670 (1985); 108 2481, 3150 (1986); 112 2402, 4324 (1990); 113 7658, 9878 (1991); 115 7944, 11744 (1993); 116 4227, 4537 (1994); 117 12593 (1995)

SL 427, 451, 577 (1990); 715 (1992); 65, 853 (1993); 299 (1994); 344, 1115 (1995)

heterocyclic halides

TL 4467 (1975) (pyridine); 30 2581 (1989) (thiophene);
31 3731 (1990) (adenosine); 32 757 (1991) (pyridine);
35 9203 (1994) (pyridine); 36 6371 (1995) (adenosine)
JOMC 93 259 (1975) (thiophene)
Chem Pharm Bull 26 3843 (1978) (pyrimidine); 27 270
(1979) (quinoline, isoquinoline, acridine); 28 3488
(1980) (pyridazine); 30 1865 (1982) (pyrimidine); 34
1447 (1986) (pyrazine)
Syn 627 (1980) (pyridine); 364 (1981) (pyridine,
quinoline, isoquinoline, cinnoline, quinoxaline); 312
(1983) (pyridine, quinoline, isoquinoline, pyridazine,
pyrimidine, pyrazine)
Heterocycles 19 329 (1982) (pyrazine)
JOC 50 2462 (1985) (pyridine); 52 2469 (pyridine),
3997 (pyrazine, pterin), 5243 (thiophene)
(1987); 53 386 (1988) (pyridine); 54 3618
(1989) (pyridine, deazapterin); 56 1816
(pyrazine, pterin), 6937 (guanine) (1991);
57 1653 (1992) (pyrrole); 60 748 (1995)
(pyridazine)
Tetr 41 621 (1985) (thiophene)
SL 755 (1990) (thiophene); 1115 (1995) (thiophene, 1H-
pyrazole, pyrimidine)

ArO₃SR_f

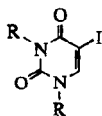
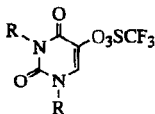
TL 27 1171 (1986); 30 2581 (1989); 34 5635, 6403
(1993)
JACS 113 9878 (1991); 114 655 (1992); 115 7944 (1993)
Syn Commun 23 1489 (1993)
JOC 59 1216, 6084 (1994)

Het-OTf

JOC 53 386 (1988) (pyridine); 60 5069 (1995) (nucleo-
side)
SL 589 (1994) (pyridine, quinoline, isoquinoline); 1115
(1995) (pyridine)
TL 35 9203 (1994) (pyridine)

RCH=CHX

TL 4467 (1975); 22 315, 421 (1981); 26 3811 (1985); 27
2033, 3589, 5857 (1986); 28 1127, 1649, 3857, 3959,
4875, 4879, 5751, 5849 (1987); 29 753 (1988); 30
2581, 6997 (1989); 31 1369, 3731 (1990); 32 69,
3171, 3391, 4363, 6109 (1991); 33 2535, 2681 (1992);
34 3663, 3679, 6403 (1993); 35 3543, 4711 (1994); 36
3687, 4245, 5891, 7225 (1995)
JOMC 93 253, 259 (1975)
Syn Commun 11 917 (1981)
J Chem Res (S) 93 (1982)
Agric Biol Chem 46 717 (1982)
Tetr 38 631 (1982)
JACS 106 3548, 5734 (1984); 107 7515 (1985); 108
5589 (1986); 109 1879 (1987); 110 631, 1626, 6921
(1988); 111 3717 (1989); 112 5875, 7410, 9330
(1990); 113 3106, 3873 (1991); 114 1450, 2544, 3120,
9369 (1992)

R'X $\text{RCH}=\text{CHO}_3\text{SCF}_3$  $\text{R}_2\text{C}=\text{C}=\text{CHBr}$ $\text{RC}\equiv\text{CBr(l)}$ $\text{R}''\text{COCl}$ ($\text{R}' = \text{R}''\text{CO}$; $\text{R}'' = \text{alkyl, aryl, 1-alkenyl, NMe}_2$)

CC 1816 (1986)

JOC 53 2655 (1988); 54 3420, 5527 (1989); 55 5324 (1990); 57 651, 3203, 3846 (1992); 58 3953, 4202, 5690, 5952, 6556, 7180 (1993); 59 4738 (1994)
 SL 715, 766 (1992); 217, 693 (1993); 713 (1994); 931 (1995)

JACS 112 4324 (1990)

JOC 50 2302 (1985); 57 3846, 4374 (1992); 58 118, 124, 1895 (1993); 60 2656 (1995)
 TL 27 1523 (1986); 29 1203 (1988); 30 2581 (1989); 31 2323 (1990); 32 1449, 1453, 3405 (1991); 34 4177, 6403, 6549 (1993); 35 1965 (1994); 36 5167, 6371 (1995)

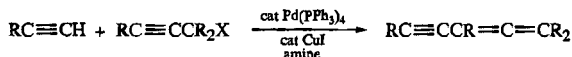
JACS 110 649 (1988); 113 3873, 6958 (1991)
 SL 409 (1991); 65 (1993); 51 (1994)

Heterocycles 26 355 (1987)
 JOC 58 6614 (1993)

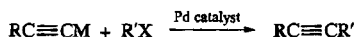
TL 29 3651 (1988)

TL 31 7227 (1990); 34 5043 (1993); 36 8087 (1995)
 JACS 112 9330 (1990)
 JOC 60 6829 (1995)

Syn 777 (1977)

 $\text{X} = \text{Cl, Br, OTs, OAc}$

TL 34 3853 (1993)

M MgX  AlEt_2 SnR_3 R'X ArX $\text{RCH}=\text{CHX}$ $\text{ArX, RCH}=\text{CHX}$ $\text{RCH}=\text{CROPO(OR)}_2$

—

JOMC 118 349 (1976)

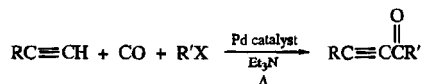
See page 585, Section 1.

TL 36 2401 (1995)

TL 21 2531 (1980); 22 1609 (1981)
 BCSJ 57 108 (1984)

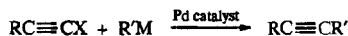
See page 592, Section 6.

Cu	ArX	JACS 107 1028 (1985) See also page 599, Section 11 for related reactions.
ZnX	RCH=CHX	CC 683 (1977) TL 27 4351, 5533 (1986); 29 2239 (1988); 30 6555 (1989); 31 2295, 4393 (1990); 32 3329 (1991); 33 6839 (1992); 34 1437 (1993); 35 9173 (1994); 36 2469, 2765 (1995)
	ArX	JACS 108 4685 (1986) JOC 59 4738 (1994) SL 524 (1994); 344 (1995) JOC 43 358 (1978) JACS 108 3403 (1986); 116 11723 (1994)
	ArO ₃ SR _f	TL 34 5333 (1993) TL 28 2387 (1987)



R' = aryl, 2-thienyl, vinylic

CC 333 (1981)



R'M

RMgX

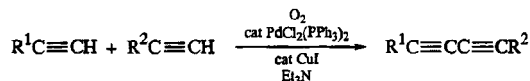
JOC 51 3772 (1986)

RCH=CRSnR₃

See page 373, Section 9.

RCH=CHZnX

SL 886 (1992)



TL 32 2797 (1991)

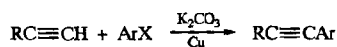
11. Organocopper Compounds

See also page 589, Section 2, and page 596, Section 10.

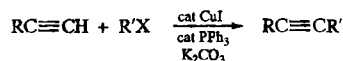
Reviews:

Tetr 40 1433 (1984)

Org Prep Proc Int 27 127 (1995)



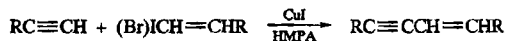
Bull Acad Sci USSR, Div Chem Sci 2539 (1968); 1079 (1970); 1209, 1488 (1971)



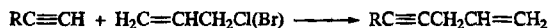
R' = aryl, vinylic; X = Br, I

TL 33 5363 (1992)

JOC 58 4716 (1993)



Syn Commun 19 2199 (1989)



cat CuCl, phase transfer catalyst, NaOH

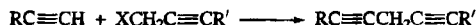
JOC 57 2188 (1992)

cat CuI, cat *n*-Bu₄NCl(Br), Na₂CO₃ or K₂CO₃

TL 30 2225 (1989); 35 4505 (1994)

cat CuI, Et₃N

TL 31 5161 (1990)



cat CuCl

TL 31 7615 (1990)

cat CuCl, NH₃

BSCF 913 (1974)

CuI, DBU or DBN

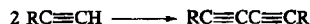
Ann 658 (1978)

CuI, *n*-Bu₄NCl, Na₂CO₃

TL 33 5757 (1992)

CuI, NaI, K₂CO₃

TL 34 4305 (1993)



Reviews:

Russ Chem Rev 32 229 (1963)

Adv Org Chem 4 225 (1963)

cat CuCl, NH₄Cl, H₂O, O₂

Adv Org Chem 4 225 (1963) (review)

JOC 29 2051 (1964)

cat CuCl, cat TMEDA, acetone, O₂

JOC 27 3320 (1962)

JACS 113 6943 (1991); 116 9019 (1994)

CuCl, NH₄Cl, NH₃, H₂O, O₂

JCS 1998 (1952)

CuCl, cat TMEDA, O₂

Org Syn Coll Vol 8 63 (1993)

CuCl, TMEDA, O₂

JOC 59 1294 (1994)

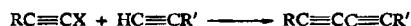
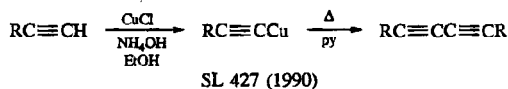
CuCl, py, O₂

JACS 113 7658 (1991)

CuCl, py, MeOH

SL 1215 (1995)

CuBr, py, O ₂ , DBU	JACS 116 7588 (1994)
cat CuI, TMEDA, O ₂	JACS 112 7405 (1990)
cat CuI, cat PdCl ₂ (PPh ₃) ₂ , O ₂ , Et ₃ N	SL 453 (1990); 859 (1995) Heterocycles 39 67 (1994)
cat CuCl ₂ , O ₂	JOC 59 2282 (1994)
cat Cu(OAc) ₂ ·H ₂ O, py, O ₂	JOC 25 1275 (1960); 57 1777 (1992) Adv Org Chem 4 225 (1963) (review) Org Syn Coll Vol 6 68 (1988) JACS 112 3910, 8931 (1990) (both intramolecular); 113 5547 (1991)
Cu(OAc) ₂ ·H ₂ O, py	JACS 111 3640 (1989) (intramolecular)
Cu(OAc) ₂ , py, Et ₂ O, O ₂	TL 35 4711 (1994)
Cu(OAc) ₂ ·py, MeOH, O ₂	Chem Ind 737 (1956) JCS 1151 (1964)
Cu(OAc) ₂ , py, MeOH, Et ₂ O, O ₂	JCS 889 (1959) TL 35 1259 (1994)



cat CuCl, NH ₂ OH·HCl, RNH ₂	Adv Org Chem 4 225 (1963) (review) J Chem Res (S) 199 (1982) Agric Biol Chem 46 717 (1982) JACS 113 5547, 6943, 9803 (1991); 114 3247 (1992) TL 33 5355 (1992) JOC 59 1236 (1994)
CuCl, TMEDA, O ₂	JOC 53 2489 (1988)
CuI, O ₂ , TMEDA	TL 34 2071 (1993)



R ₂ C=CHCH ₂ OMs, cat Li ₂ CuCl ₄	JACS 108 806 (1986)
RCH=CRCH ₂ Cl, cat Li ₂ CuCl ₄	JACS 111 989 (1989)
RCH=CHCH ₂ Cl, cat CuCl	TL 31 5749 (1990)
RC≡CCMe ₂ Cl, cat CuCl	JACS 107 6546 (1985)
RC≡CCH ₂ Br, CuCl	Biochim Biophys Acta 144 296 (1967) Org Syn Coll Vol 6 925 (1988) TL 31 4033 (1990)
RC≡CCH ₂ Br, CuCN	TL 31 4033 (1990)

R'X

ArX

Russ Chem Rev 37 748 (1968) (review)
 Bull Acad Sci USSR, Div Chem Sci 2043 (1963)
 JOC 28 2163, 3313 (1963); 30 3857 (1965); 31 4071
 (1966); 42 2626 (1977); 52 1339 (1987)
 JACS 86 4358 (1964); 88 3027 (1966); 91 6464
 (1969); 113 5547 (1991)
 Chem Ind 2101 (1964)
 JCS C 578 (1967); 2173 (1969)
 CC 718 (1967)
 J Label Compds 6 197 (1970)

RCH=CHX

CC 1259 (1967)
 JOC USSR 4 21 (1968)
 JOMC 93 415 (1975)
 JOC 47 2109 (1982)

 $\text{H}_2\text{C}=\text{CHCH}_2\text{X}$

Bull Acad Sci USSR, Div Chem Sci 2043 (1963)
 JACS 91 6464 (1969); 109 3684 (1987)
 (NaCN added)
 Compt Rend 270 354 (1970)
 BSCF 913 (1974)
 Ann 658 (1978)
 JOC 60 139 (1995)

 $\text{RC}\equiv\text{CBr}$

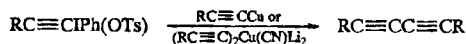
Compt Rend 241 1055 (1955)
 JACS 116 7588 (1994)

 $\text{RC}\equiv\text{CCH}_2\text{Br(I)}$

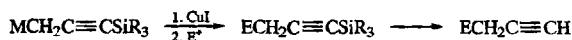
JOC 54 500 (1989); 57 1952 (1992)

 $\text{Me}_3\text{SiC}\equiv\text{CCH}_2\text{I}$

TL 28 3547 (1987)



JOC 59 8053 (1994)

ME⁺

Li

RCHO

JACS 109 5437 (1987)

MgBr

 $\text{R}_2\text{C}=\text{CHCH}_2\text{Cl}$

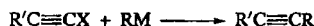
JOC 52 3860, 3883 (1987)

 $\text{R}_2\text{C}=\text{CRCH}_2\text{OPO(OEt)}_2$

TL 28 527, 723 (1987)


JACS 106 6006 (1984)

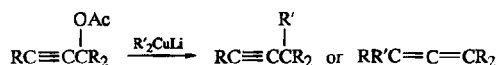
TL 28 527 (1987)



X = Br, I

RM

ArCu	TL 5209 (1972); 1441 (1978)
RCu·MgBr ₂ (R = alkyl, vinylic)	TL 1466 (1975) Tetr 36 1215 (1980)
R ₂ CuLi	JOMC 251 133 (1983)
RCu(CN)Li	JOMC 251 133 (1983)
RCu(CN)ZnX	TL 30 4799 (1989); 31 1833, 7597 (1990); 36 1023 (1995) JOC 56 5974 (1991)
RCO ₂ CHRCu(CN)ZnBr	JOC 54 5202 (1989); 55 4791 (1990); 58 588 (1993)
RSCHRCu(CN)ZnCl	TL 31 7575 (1990)
 NCH ₂ Cu(CN)ZnX	JOC 58 588 (1993)
RO ₂ CCH(NHBoc)CH ₂ Cu(CN)ZnI	SL 499 (1993) JOC 60 2210 (1995)
RCH=CHZnX, CuCN·2LiCl	JOC 56 4593 (1991)
R ₂ Zn, CuCN·2LiCl	JOC 57 1956 (1992) TL 34 5261 (1993)
RCH=CHTeBu / Me ₂ Cu(CN)Li ₂ / ZnCl ₂	SL 1145 (1995)



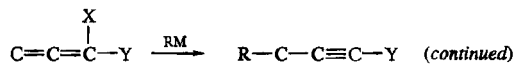
CC 876 (1978)
JOC 45 4740 (1980)



TL 31 3703 (1990)



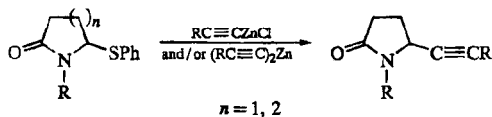
<u>X</u>	<u>Y</u>	<u>RM</u>	
Br	H	PhCu·MgBr ₂ ·LiBr (PhCuBr)MgBr·LiBr, (RCuBr)MgX·LiBr, RCu(CN)Li (R = 1° alkyl)	JOC 52 3920 (1987) TL 28 6073 (1987)
		R ₂ Cu(CN)Li ₂	TL 35 7775 (1994)
	alkyl	Me ₃ Cu ₂ Li, MeCu·n-Bu ₃ P, RCu(CN)Li (R = 1°, 2° alkyl; aryl)	TL 25 3059 (1984)
		RCH=CHLi, CuCN	JOC 51 2230 (1986)
		RC≡CCu(CN)Li	JACS 103 4618 (1981)



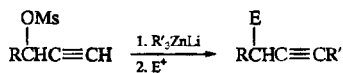
<u>X</u>	<u>Y</u>	<u>RM</u>	
I	alkyl	$\text{RCH}=\text{CHCu}$	TL 23 1651 (1982)
		$\text{ArCu}(\text{CN})\text{Li}$	TL 24 3291 (1983)
	OMe	RMgX, CuBr	JOC 45 1158 (1980)
OMe	H	$\text{RMgX}, \text{CuX} (\text{X} = \text{Cl}, \text{Br}, \text{I})$	Rec Trav Chim 93 183 (1974)

12. Organozinc Compounds

See also page 596, Section 10 and page 599, Section 11.



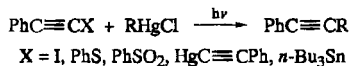
TL 29 5391 (1988)



$\text{E}^+ = \text{NCS}, \text{I}_2, \text{Me}_3\text{SiCl}, \text{RCOCl}, \text{RCHO} (\text{ZnCl}_2)$

JOC 58 6166 (1993)

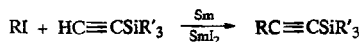
13. Organomercury Compounds



TL 27 3479 (1986)

JACS 110 3530 (1988)

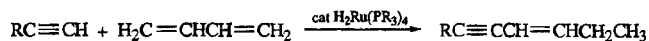
14. Organosamarium Compounds



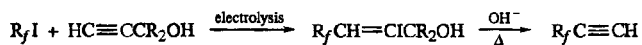
$\text{R} = 1^\circ, 2^\circ \text{ alkyl; vinylic}$

SL 179 (1994)

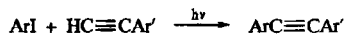
15. Miscellaneous Reactions



CC 496 (1981)



CC 433 (1982)



Ar = furan, thiophene

JOC 55 4019 (1990)

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W. A. Thaler, "Methods in Free Radical Chemistry," Ed. E. S. Huyser, Marcel Dekker, New York (1969), Vol 2, pp 121-227
Syn 7 (1970)

1. Aliphatic Halogenation



Fluorination

F₂

JACS 98 3034, 3036 (1976); 113 5475 (1991)
TL 21 5067 (1980); 25 1947 (1984); 26 2793 (1985)
Nouv J Chim 4 239 (1980)
J Fluorine Chem 20 689 (1982)
JOC 51 3522 (1986); 52 2769, 4928 (1987); 53 78, 2803 (1988); 54 1990 (1989); 55 5933 (1990); 57 4749 (1992); 58 1704 (1993); 59 4332 (1994)

ClF₃

JOC 52 798 (1987)

CF₃OF

JACS 92 7494 (1970); 98 3034, 3036, 5591 (1976)
Nouv J Chim 4 239 (1980)

Chlorination

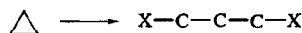
- Cl₂ JACS 79 2977 (1957); 80 4987, 4997 (1958);
81 1485 (1959); 105 120 (1983); 107 2823,
5464 (1985); 108 6300 (1986); 110 3519,
3525 (1988); 111 3652 (1989); 113 5397
(1991)
JCS 144 (1960)
JOC 52 1155 (1987); 53 305 (1988); 54 2051
(1989)
Acct Chem Res 23 219 (1990)
- Cl₂, hv, zeolite JOC 53 3731 (1988)
- SO₂Cl₂ JACS 61 2142 (1939); 62 927 (1940)
JCS 1851 (1951)
Org Syn Coll Vol 6 271 (1988)
- SO₂Cl₂, cat Co(II)-porphyrin TL 35 5935 (1994)
- Cl₃CSO₂Cl JACS 82 5246 (1960)
- NCS JOC 18 649 (1953)
- C₆H₅ICl₂ JOC 29 3692 (1964); 32 1517 (1967)
CL 961 (1979)
TL 33 4145 (1992)
- t*-C₄H₉OCl JACS 89 4891, 4895 (1967)
- PCl₅ Angew 77 506 (1955)
- R₂NCl, CF₃CO₂H, FeSO₄·7H₂O JOC 44 3728 (1979)
- CH₂Cl₂, SbF₅ JOC 54 1463 (1989)

Bromination

- Br₂ JCS 144 (1960)
Rec Trav Chim 83 67 (1964)
JACS 110 1303 (1988)
- Br₂, AlBr₃ JOC 58 5560 (1993)
- Cl₃CSO₂Br JOC 30 38 (1965)
- NBS JCS 2240 (1952)
JOC 18 649 (1953)
- (C₆H₅)₂C=NBr JOC 32 223 (1967)
- CH₂Br₂, SbF₅ JOC 54 1463 (1989)

Iodination

- t*-C₄H₉OI JACS 90 808 (1968)



X

Reagent(s)

Cl

 $\text{Cl}_2, h\nu$

IACS 84 3326 (1962); 94 301 (1972)

IOC 41 523 (1976)

Br

 Br_2

IACS 61 2139 (1939); 95 856 (1973)

IOC 37 4082 (1972); 41 671 (1976)

 $\text{Br}_2, h\nu$

IACS 60 217 (1938); 95 6728 (1973); 112 5557 (1990)

IOC 41 523 (1976)

 Br_2, HBr

J Prakt Chem 62 273 (1900)

 Br_2, NBS

IACS 98 1195 (1976)

IOC 41 671 (1976)

 $\text{Br}_2, \text{cat FeBr}_3$

IOC 41 671 (1976)

I

 I_2

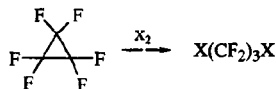
IACS 60 217 (1938)

J Chem Phys 7 736 (1939); 34 521 (1961)

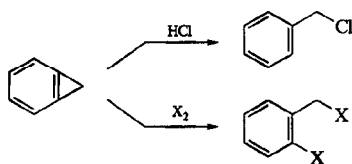
TL 27 1553 (1986)

 $\text{I}_2, h\nu$

J Chem Phys 7 736 (1939); 34 521 (1961)

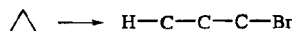

 $\text{X} = \text{Cl}, \text{Br}, \text{I}$

IACS 117 5397 (1995)


 $\text{X} = \text{Br}, \text{I}$

IACS 102 7076 (1980)

IOC 53 1312 (1988)

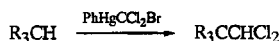


HBr

IACS 61 2139 (1939)

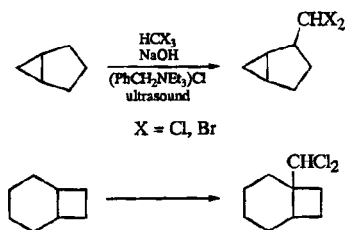
 HBr, Br_2

IACS 98 1195 (1976)



IOC 35 1989 (1970)

IACS 93 4072 (1971)

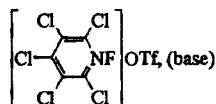


JACS 114 783 (1992)

2. Allylic Halogenation



Fluorination



JACS 112 8563 (1990)

PhSeF/ O_3

TL 31 973 (1990)

Chlorination

 $\text{C}_6\text{H}_5\text{SO}_2\text{NCIC}_6\text{H}_{13}$

Ann 703 34 (1967)

 $t\text{-C}_4\text{H}_9\text{OCl}$

JACS 83 3877 (1961)

TL 21 781 (1980)

NCS, TsNSO

JOC 44 4204 (1979)

NCS, cat (ArSe)₂

JOC 44 4204, 4208 (1979)

 $\text{PhSeCl}_3/\text{H}_2\text{O}$, NaHCO_3

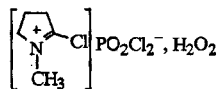
JOC 52 4086 (1987)

HOCl

TL 21 441 (1980)

 NaCl , H_2O , H_2SO_4 , CH_2Cl_2 , electrolysis

TL 22 3193 (1981)



SL 477 (1991)

Bromination

NBS

JOC 14 375 (1945); 50 2007 (1985); 60 829, 1814 (1995)

Chem Rev 43 271 (1948); 63 21 (1963) (both reviews)

JACS 73 5153 (1951); 106 3297 (1984); 108 1251 (1986); 112 228, 462 (on enol silane), 2749 (1990)

Angew 71 349 (1959) (review)

Org Syn Coll Vol 4 108 (1963)

Newer Methods Prep Org Chem 3 151 (1964)

TL 31 7509 (1990)

$(C_6H_5)_2C=NBr$

JOC 32 223 (1967)

$(C_3H_5NH)Br_3$, py

TL 29 6835 (1988)

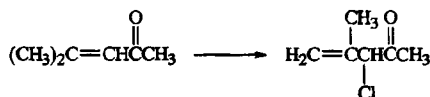


Cl_2

TL 33 495 (1992)

$HOCl$

TL 21 441 (1980)

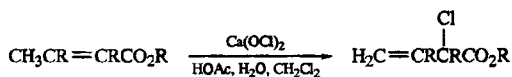


$HOCl$

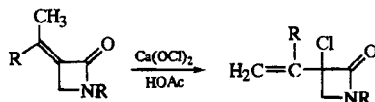
TL 22 5019 (1981)

$Ca(OCl)_2$, HOAc

JOC 56 713 (1991)

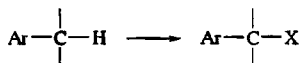


JOC 55 3880 (1990); 57 2753 (1992)



CC 735 (1987)

3. Benzylic Halogenation



Fluorination

CF_3OF

JACS 92 7494 (1970)

$CsSO_4F$

JOC 56 7347 (1991)


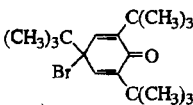
AgF , TiO_2 , hv

JACS 112 2016 (1990)

Chlorination

- NCS TL 34 5725 (1993)
- SO₂Cl₂ JACS 61 2142 (1939)
JCS 1851 (1951)
Tetr 25 4363 (1969); 26 2041 (1970)
TL 34 5725 (1993)
JOC 58 964 (1993)
- SO₂Cl₂, cat Pd(PPh₃)₄ CL 223 (1978)
- SO₂Cl₂, zeolite JOC 55 5260 (1990)
- Cl₂, PCl₅ Org Syn Coll Vol 2 133 (1943)
- PCl₅ JOC 34 3655 (1969)
- C₆H₅ICl₂ JOC 29 3692 (1964)
- (PhCH₂NMe₃)ICl₄, AIBN TL 29 5783 (1988)
- t*-C₄H₉OCl JACS 82 6108, 6113 (1960); 89 4885, 4891, 4895 (1967)

Bromination

- Br₂ Org Syn Coll Vol 2 443 (1943); 3 788 (1955); 4 984 (1963)
JACS 112 2736 (1990)
TL 34 5725 (1993)
- Br₂-N--polymer JOC 51 929 (1986)
- Br₂, cat La(OAc)₃ BSCF II 327 (1982)
- Br₂, NBS JACS 112 7369 (1990)
- (C₅H₅NH)Br₃ JOC 57 2316 (1992)
- NBS Chem Rev 43 271 (1948); 63 21 (1963)
(both reviews)
Angew 71 349 (1959) (review)
Org Syn Coll Vol 4 921 (1963)
JOC 50 2128, 2557, 2939 (1985); 51 3407 (1986); 58 964, 7498 (1993); 59 4473 (1994)
JACS 110 8153 (1988); 112 2736 (1990)
TL 33 1237 (1992)
- BrCCl₃ JACS 82 391 (1960)
JOC 55 4469 (1990)
- CBr₄ JACS 54 2025 (1932)
- (C₆H₅)₂C=NBr JOC 32 223 (1967)
-  Tetr 25 4357 (1969)

NH_4Br , O_2 , cat $(\text{NO})\text{BF}_4$

JOC 53 3548 (1988)

 CuBr_2 , $t\text{-BuO}_2\text{H}$, Ac_2O

Syn Commun 11 669 (1981)

Iodination

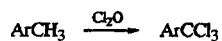
 $t\text{-C}_4\text{H}_9\text{OI}$

JACS 90 808 (1968)



SL 531 (1992)

JACS 114 6227 (1992)



JACS 104 4680 (1982)

2. AROMATIC HALOGENATION

See page 703, Section 9, for substitution of aromatic OH by halogen.



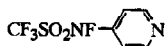
Reviews:

- E. T. McBee and H. B. Hass, *Ind Eng Chem* **33** 137 (1941)
 P. H. Groggins, "Unit Processes in Organic Synthesis," McGraw-Hill, New York (1958), p 204
 P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution, Nitration and Halogenation," Butterworths Scientific Publications, London (1959)
 H. P. Braendlin and E. T. McBee, "Friedel-Crafts and Related Reactions," Ed. G. Olah, Interscience Publishers, New York (1964), Vol III, Pt 2, p 1517
 R. O. C. Norman and R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, New York (1965), pp 119-155
 P. B. D. de la Mare, "Electrophilic Halogenation," Cambridge University Press, Cambridge (1976)

Fluorination

review	<i>Chem Eng News</i> , July 9, 72 (1962)
F ₂	<i>JOC</i> 35 723, 4020 (1970); 56 142 (1991) <i>TL</i> 28 255 (1987) (pyridines)
F ₂ , HF	<i>J Nucl Med</i> 25 1228 (1984)
F ₂ , HF, BF ₃ ·OEt ₂	<i>J Nucl Med</i> 27 417 (1986)
F ₂ , BCl ₃ or AlCl ₃	<i>JOC</i> 56 142 (1991)
XeF ₂	<i>Israel J Chem</i> 17 71 (1978)
XeF ₂ , HF	<i>JACS</i> 91 1563 (1969)
CF ₃ OF	<i>CC</i> 806 (1968) <i>JACS</i> 92 7494 (1970) <i>JCS Perkin I</i> 2889 (1972) <i>Anal de Quim</i> 70 871 (1974) <i>JOC</i> 39 2120 (1974); 41 3413 (1976) <i>Israel J Chem</i> 17 60 (1978)

$\text{CH}_3\text{CO}_2\text{F}$	JOC 49 806 (1984); 60 227 (1995) TL 31 619 (1990)
$\text{CF}_3\text{CO}_2\text{F}$	JOC 46 4629 (1981); 49 806 (1984) J Nucl Med 27 1462 (1986) Appl Radiat Isot 37 877 (1986)
$\text{Hg}(\text{O}_2\text{CCF}_3)_2 / \text{CH}_3\text{CO}_2\text{F}$	TL 29 1501 (1988)
$\text{Ti}(\text{O}_2\text{CCF}_3)_3 / \text{KF} / \text{BF}_3$	JOC 42 362 (1977)
CsSO_4F	JACS 103 1964 (1981)
CsSO_4F , cat BF_3	CC 148 (1981) Tetr 40 189 (1984) JOC 50 3609 (1985); 51 3242 (1986)



J Fluorine Chem 46 297 (1990)

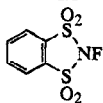


JACS 109 7194 (1987)

JOC 57 1536 (1992)

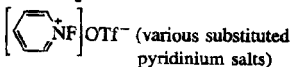


SL 189 (1991)



TL 32 1631 (1991)

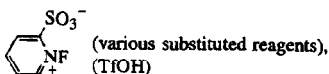
JOC 60 4730 (1995)



TL 27 4465 (1986)

JOC 54 1018 (1989)

JACS 112 8563 (1990)





JOC 60 6563 (1995)

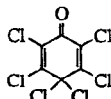


JOC 58 2791 (1993)

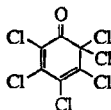
Chlorination

Cl_2	JOC 50 2145 (1985) (phenols)
Cl_2 , H_2O	TL 28 4805 (1987) (aryl ethers)
Cl_2 , $(\text{MeO})_3\text{PO}$	Syn 621 (1976)
Cl_2 , silica	TL 3395 (1974) CL 1423 (1980)
Cl_2 , FeCl_3	CL 1423 (1980)
CH	JOC 59 6233, 7335 (1994)
SO_2Cl_2	Org Syn Coll Vol 3 267 (1955) (phenol) Austral J Chem 28 1113 (1975) (phenol) JOC 46 4486 (1981); 50 2145 (1985); 52 4485 (1987) (all phenols only); 60 1565 (1995) TL 23 4569 (1982) (phenol)

SO ₂ Cl ₂ , cat amine	TL 36 3893 (1995) (phenol)
SO ₂ Cl ₂ , cat (PhS) ₂ , cat AlCl ₃	TL 2591 (1976) (phenols) JOC 50 2145 (1985) (phenols)
SO ₂ Cl ₂ , cat (PhS) ₂ , cat FeCl ₃	JOC 50 2145 (1985) (phenols)
SO ₂ Cl ₂ , silica	Syn Commun 5 169 (1975)
SO ₂ Cl ₂ , zeolite	JOC 55 5260 (1990)
S ₂ Cl ₂ , SO ₂ Cl ₂ , AlCl ₃	JCS 127 2677 (1925) IACS 82 4254 (1960); 115 1285 (1993)
TiCl ₄ , CF ₃ CO ₂ H	TL 2611 (1970)
CuCl ₂	JOC 26 2263, 2267 (1961) JCS 1216 (1963) Tetr 25 1591 (1969) Org Syn Coll Vol 5 206 (1973)
CuCl ₂ , alumina	JOC 53 2093 (1988)
CuCl ₂ , O ₂ , HCl	JCS C 1982 (1970) (phenols, anilines)
Cl ₂ O, H ₂ SO ₄ or CF ₃ SO ₃ H	IACS 104 4680 (1982)
Cl ₂ O, POCl ₃ , Tf ₂ O	Ber 112 1677 (1979)
NaOCl, HOAc	JCS 1056 (1909) IACS 108 1000 (1986)
Ca(OCl) ₂	TL 33 777 (1992)
<i>t</i> -BuOCl, silica	Syn 1155 (1985)
<i>t</i> -BuOCl, zeolites	Syn 1157 (1985)
<i>t</i> -BuOCl, micelles	CC 833 (1982) (phenols)
R ₂ NCl, silica	TL 29 1319 (1988) (phenols)
 NCl, CF ₃ CO ₂ H	TL 24 3117 (1983) JCS Perkin II 1533 (1987); 385 (1988)
R ₂ NCl, CF ₃ CO ₂ H	JCS Perkin II 385 (1988); 1529 (1989)
 NCl, H ₂ SO ₄	Org Syn Coll Vol 8 167 (1993)
(R ₃ NCl)X (X = Cl, ClO ₄ , OAc), CF ₃ CO ₂ H	TL 24 3117 (1983) JCS Perkin II 1533 (1987); 385 (1988)
NCS, HClO ₄	JOC 58 3072 (1993)
NCS, H ₂ SO ₄	JOC 30 304 (1965)
NCS, TsOH	Syn 237 (1993)
NCS, HOAc	JOC 59 5543 (1994)
NCS, cat Amberlyst 15	J Mol Catal 88 377 (1994)
PhI(OH)OTs, LiCl or NaCl	TL 35 2841 (1994)



CC 8 (1980) (phenols)



CC 8 (1980) (phenols)

Bromination Br_2 vapor

Org Syn Coll Vol 4 256 (1963)

 Br_2 , CH_2Cl_2

JOC 52 3312 (1992)

TL 36 1705 (1995)

 Br_2 , CCl_4 Org Syn Coll Vol 1 121 (1941); 2 95 (1943);
3 134 (1955); 5 147 (1973) Br_2 , CS_2

Org Syn Coll Vol 4 128 (1941)

 Br_2 , $(\text{MeO})_3\text{PO}$

Syn 621 (1976)

 Br_2 , H_2O

JOC 52 4485 (1987)

 Br_2 , H_2O , H^+

Org Syn Coll Vol 2 97, 592 (1943); 4 947 (1963)

 Br_2 , HOAc Org Syn Coll Vol 2 100, 173 (1943)
JOC 52 4485 (1987); 60 1565 (1995) Br_2 , HOAc , NaOAc

JOC 52 4485 (1987)

 Br_2 , HF , SbF_5

CC 110 (1980) (meta, phenols, aryl ethers)

 Br_2 , KBr , H_2O

JOC 52 4485 (1987)

 Br_2 ; H_2O , MeOH or HCCl_3 ; LiBr ,
 $n\text{-Bu}_4\text{NBr}$ or $(n\text{-C}_{12}\text{H}_{26}\text{NMe}_3)\text{Br}$

TL 30 6209 (1989) (anilines)

 Br_2 , Et_4NCl , MeOH

TL 34 2115 (1993) (anilines)

 Br_2 , H_2O_2 , $n\text{-Bu}_4\text{NBr}$

CC 1421 (1987)

 Br_2 , $i\text{-BuNH}_2$ JOC 32 2358 (1967); 58 3877 (1993); 60 4542
(1995) (all phenols)
JACS 108 806 (1986) Br_2 , silica

TL 3395 (1974); 27 1051 (1986) (heterocycles)

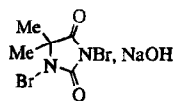
 Br_2 , cat I_2

JACS 115 5422 (1993)

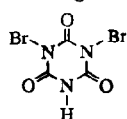
 Br_2 , AlCl_3 Helv 29 1144 (1946)
Org Syn Coll Vol 5 117 (1973) Br_2 , $\text{Ti}(\text{OAc})_3$ TL 1623 (1969)
JOC 37 88 (1972) Br_2 , Fe Org Syn Coll Vol 1 123 (1941); 3 138 (1955);
4 114 (1963) Br_2 , FeCl_3

Helv 29 1144 (1946)

Br ₂ , AgO ₃ SR	Syn 693 (1978)
Br ₂ , AgNO ₃ , HOAc, HNO ₃	JCS 573 (1950)
Br ₂ , AgSO ₄ , H ₂ SO ₄	JCS 573 (1950)
Br ₂ , ZnCl ₂	Helv 29 1144 (1946)
Br ₂ , Hg(NO ₃) ₂ , HOAc	JCS 573 (1950)
Br ₂ , HgO, H ₂ SO ₄	JOC 53 1799 (1988)
Br ₂ , KBrO ₃ , HOAc, H ₂ SO ₄	JCS 573 (1950)
Br ₂ , BrF ₃	JOC 58 239 (1993)
BrF	JOC 53 5545 (1988)
DBU·HBr ₃	JOC 57 2740 (1992)
NaBr or KBr, HF, SbF ₅	TL 31 2007 (1990) (aryl ethers)
KBr, H ₂ O ₂ , cat NH ₄ VO ₃ , H ₂ O, HCCl ₃	TL 35 7429 (1994) (aryl ethers)
KBr, H ₂ O ₂ , cat (NH ₄) ₆ Mo ₇ O ₂₄ , HOAc	SL 450 (1994)
KBr, <i>m</i> -ClC ₆ H ₄ CO ₃ H, cat 18-crown-6	JCS Perkin I 1423 (1987) (aryl ethers, phenols)
KBrO ₃ , H ₂ SO ₄	JOC 46 2169 (1981)
HOBr, HClO ₄ or H ₂ SO ₄	JCS 997 (1962)
HOBr, HOAc	JCS 2317 (1954)
HBr, H ₂ O ₂ , <i>n</i> -Bu ₄ NBr	CC 1421 (1987)
Hg(OAc) ₂ /Br ₂	JCS 637 (1926)
CuBr ₂	JOC 26 2263 (1961) JCS 1216 (1963) JACS 86 427 (1964) Tetr 25 1591 (1969)
CuBr ₂ , alumina	JOC 53 2093 (1988)
NBS	JACS 80 4327 (1958) JOC 30 304 (1965); 44 4733 (1979); 57 2316 (1992); 59 4473, 5543 (1994); 60 4412, 5328 (1995)
NBS, Al ₂ O ₃ -SiO ₂	TL 35 7055 (1994)
NBS, SiO ₂	BCSJ 62 591 (1989)
NBS, HClO ₄	JOC 58 3072 (1993)
NBS, H ₂ SO ₄	JOC 30 304 (1965)
NBS, TsOH	Syn 237 (1993)
NBS, cat PhI(OH)OTs	Syn 237 (1993)
NBS, cat Amberlyst 15	J Mol Catal 88 377 (1994)
NBS, NaOH	TL 34 931 (1993)



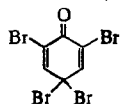
TL 34 931 (1993)

CBr₄

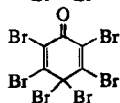
JACS 54 2025 (1932)

hexabromocyclopentadiene

CC 778 (1982)



Org Syn Coll Vol 6 181 (1988)



JCS C 3652 (1971) (anilines)

Chim Ind (Milan) 53 467 (1971) (phenols)

Iodination

reviews

Russ Chem Rev 53 343 (1984)

Syn 923 (1988)

I₂

Org Syn Coll Vol 2 347 (1943)

BCSJ 39 128 (1966)

TL 27 5963 (1986)

I₂, DMSO

JOC USSR 12 1568 (1976)

I₂, (MeO)₃PO

Syn 621 (1976)

I₂, alumina

TL 27 2207 (1986)

JOC 53 4477 (1988)

I₂, HNO₃

Org Syn Coll Vol 1 323 (1932)

I₂, NaNO₂, H₂SO₄

JACS 65 1273 (1943)

I₂, SO₃, H₂SO₄

Org Syn Coll Vol 3 796 (1955)

JCS C 1480 (1970)

I₂, HIO₃

Tetr 32 503 (1976)

I₂, HIO₃, H₂SO₄, HOAc

JOC 55 2696 (1990)

I₂, HIO₄·2H₂O, H₂SO₄

JOC 49 3051 (1984); 56 5903 (1991)

I₂, HIO₄·2H₂O, HOAc

CC 1476 (1987)

I₂, HIO₄·2H₂O, H₂SO₄, HOAc

BCSJ 39 128 (1966)

Org Syn Coll Vol 6 700 (1988)

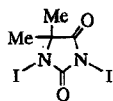
JOC 56 3192 (1991); 59 5414 (1994); 60 7953 (1995)

I₂, NaIO₃, H₂SO₄, HOAc

JOC 59 4206 (1994)

I ₂ , KIO ₃ , H ₂ SO ₄	JACS 65 1273 (1943)
I ₂ , PhI(O ₂ CCF ₃) ₂	Syn 486 (1980) JOC USSR 17 2320 (1981)
I ₂ , PhI(OH)OTs	SL 131 (1992)
I ₂ , AlCl ₃ , CuCl ₂	CL 1481 (1982)
I ₂ , CuCl ₂	JOC 35 3436 (1970)
I ₂ , Cu(OAc) ₂ , (NH ₄) ₂ S ₂ O ₈	JOC 56 3238 (1991)
I ₂ , Ag ₂ O ₂ CCF ₃	Org Syn Coll Vol 4 547 (1963) JACS 112 6960 (1990) JOC 60 227 (1995)
I ₂ , AgClO ₄	Ber 65 395 (1932) BCSJ 39 128 (1966)
I ₂ , AgNO ₂	TL 30 3769 (1989)
I ₂ , Ag ₂ SO ₄	JCS 150 (1952) BCSJ 39 128 (1966) JOC 56 3238 (1991) TL 34 6223 (1993)
I ₂ , HgO	Org Syn Coll Vol 2 357 (1943) JACS 74 4950 (1952) BCSJ 39 128 (1966)
I ₂ , Hg(OAc) ₂	Z Naturforsch 8B 436 (1953) TL 34 7085 (1993)
I ₂ , CAN	JOC 56 3238 (1991)
I ₂ , H ₂ O ₂	JCS 3164 (1927)
I ₂ , CH ₃ CO ₂ H	Tetr 20 2751 (1964)
I ₂ , CF ₃ CO ₂ H, electrolysis	Acta Chem Scand B 34 47 (1980)
I ₂ , KI, EtNH ₂	JCS 840 (1950)
I ₂ , KI, EDA	JCS 3711 (1953)
I ₂ , KI, NH ₄ OH	JACS 67 1416 (1945) (phenols)
I ₂ , NH ₃	JACS 39 441 (1917)
I ₂ , morpholine	Compt Rend 245 174 (1957)
I ₂ , NaHCO ₃	BCSJ 38 1590 (1965)
I ₂ , KOH	JOC 49 3046 (1984) (phenols)
I ₂ , TiOAc	JCS Perkin I 1161 (1976) (phenols)
IF	JOC 53 1123 (1988); 55 3552 (1990) TL 35 9701 (1994)
ICI	Org Syn Coll Vol 2 196, 343, 349 (1943) SL 577 (1990) JOC 59 6233, 7335 (1994); 60 1565 (1995)

ICl, (MeO) ₃ PO	Syn 621 (1976)
ICl, ZnCl ₂ , HOAc	JACS 78 5623 (1956)
ICl-py	J Chem Res (S) 405 (1994)
KICl ₂	JACS 78 3210 (1956) JOC 59 1344 (1994)
(PhCH ₂ NMe ₃)ICl ₂ , CaCO ₃ or NaHCO ₃	CL 2109 (1987) (phenols) BCSJ 61 600 (1988) (anilines)
I(py) ₂ BF ₄ , CF ₃ SO ₃ H	TL 34 3893 (1993) JOC 58 2058 (1993)
I(py) ₂ BF ₄ , HBF ₄	JOC 58 2058 (1993)
I(sym-collidine) ₂ PF ₆	TL 36 8217 (1995) (phenols, anilines)
NaI, chloramine T	TL 26 2043 (1985) (phenols) JOC 59 383 (1994) (phenols)
NaI, t-BuOCl	JOC 50 5384 (1985) (phenols)
NaI, NaOCl	JOC 55 5287 (1990) (phenols)
KI, H ₂ O ₂	JCS 3164 (1927)
KI, KIO ₃	JCS 632 (1949)
KI, HIO ₄ , H ₂ SO ₄	JOC 48 4772 (1983)
KI, m-ClC ₆ H ₄ CO ₃ H, cat 18-crown-6	JCS Perkin I 1423 (1987) (aryl ethers, phenols)
NH ₄ I, O ₂ , cat (NO)BF ₄	JOC 53 3548 (1988)
n-Bu ₄ NI, O ₂ , NaNO ₃	JOC 56 3238 (1991)
MI (M = n-Bu ₄ N, Li, Na, K, I), CAN	BCSJ 54 2847 (1981) Syn Commun 20 439 (1990) SL 525 (1990)
FeI ₂ ·4H ₂ O, CuCl ₂	JOC 35 3436 (1970)
Hg(OAc) ₂ /I ₂	JOC 60 5905 (1995)
Hg(OAc) ₂ /I ₂ , KI	JOC 50 5092 (1985)
Hg(O ₂ CCF ₃) ₂ /I ₂	TL 31 4653 (1991) JACS 115 5422 (1993)
Ti(O ₂ CCF ₃) ₃ /KI	TL 2427 (1969); 31 4653 (1990) JACS 93 4841 (1971) Org Syn Coll Vol 6 709 (1988) JOC 59 383 (1994)
NIS, CF ₃ SO ₃ H	JOC 58 3194 (1993)
NIS, cat PhI(OH)OTs	SL 131 (1992)



JOC 30 1101 (1965)

XReagent

F



JACS 106 452 (1984)

Br

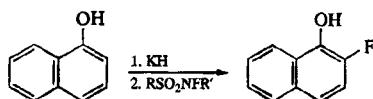


JACS 114 10715 (1992)

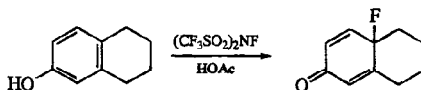
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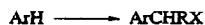
JACS 116 3988 (1994)



JACS 106 452 (1984)



JOC 57 1536 (1992)

Reviews:

Org Rxs 1 63 (1942)

Russ Chem Rev 46 891 (1977)

XReagents

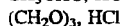
Cl

Org Syn Coll Vol 3 197, 557
(1955)

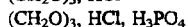
JACS 78 5423 (1956)



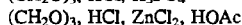
Org Syn Coll Vol 4 980 (1963)



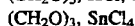
Org Syn Coll Vol 3 195 (1955)



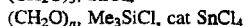
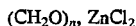
JOC 56 3192 (1991)



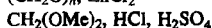
JACS 75 6292 (1953)



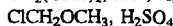
JOC 41 1627 (1976)

JACS 112 8187 (1990) (poly-
styrene)

JOC 41 1627 (1976)



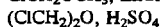
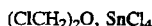
Org Syn Coll Vol 3 468 (1955)



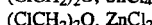
BCSJ 43 3299 (1970)



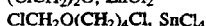
JOC 57 5243 (1992)

Rec Trav Chim Pays-Bas 87 65
(1968)

JOC 41 1627 (1976)



JOC USSR 7 1485 (1971)



Syn 560 (1974)



JOC 41 1627 (1976)



Syn 560 (1974)

JOC 41 1627 (1976)

TL 24 1933 (1983)

XReagents

Br

$(\text{CH}_2\text{O})_3$, HBr, HOAc, cat
 $(n\text{-C}_{14}\text{H}_{29}\text{NMe}_3)\text{Br}$

SL 55 (1989)

$(\text{CH}_2\text{O})_n$, HBr, HOAc

JOC 58 1262 (1993)

$(\text{CH}_2\text{O})_m$, HBr, HOAc, H_3PO_4

JACS 114 6227 (1992)

$(\text{CH}_2\text{O})_m$, Me_3SiBr , cat SnCl_4

JACS 112 8187 (1990)

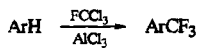
(polystyrene)

$\text{BrCH}_2\text{O}(\text{CH}_2)_4\text{Cl}$, ZnBr_2

Syn 560 (1974)

$\text{BrCH}_2\text{O}(\text{CH}_2)_4\text{OCH}_2\text{Br}$, ZnBr_2

Syn 560 (1974)



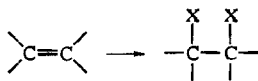
TL 30 3825 (1989)

JOC 56 103 (1990)

3. HALOGENATION OF ALKENES

See also page 410, Section 2 for the halogenation of vinylic organometallics.

1. Halogen Addition

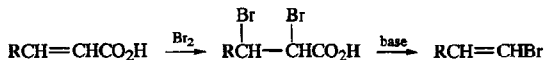


Reviews:

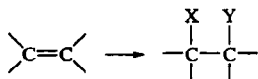
H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Inc. (1972), pp 422-429
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
 Vol 4, Part 1.8, p 329

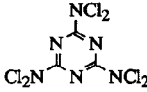
<u>X</u>	<u>Reagent(s)</u>	
F	F ₂	JOC 31 1859, 3871 (1966); 51 3607 (1986) JACS 88 1822 (1966); 89 609 (1967) JCS Perkin I 1105 (1982) TL 35 5665 (1994); 36 6705 (1995)
	XeF ₂	JACS 86 5021 (1964) JOC 42 1559 (1977); 59 5891 (1994) JCS Perkin I 2169 (1977) Israel J Chem 17 71 (1979) J Fluorine Chem 20 13 (1982)
	XeF ₂ , H ⁺	TL 1015 (1974) JOC 41 4002 (1976); 43 696 (1978); 44 1255 (1979); 49 333 (1984) Tetr 33 1017 (1977)
	XeF ₂ , BF ₃ ·OEt ₂	TL 363 (1977) JOC 49 333 (1984)
	XeF ₄	JACS 86 5021 (1964)
	CsSO ₄ F	JOC 52 919 (1987)
	CF ₃ OF	JCS Perkin I 1105 (1982)
	(CF ₃ SO ₂) ₂ NF, HF-py	JOC 57 629 (1992)

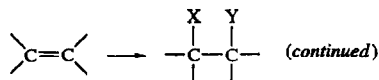
<u>X</u>	<u>Reagent(s)</u>	
F (continued)	$\left[\text{ClCH}_2\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{NF} \right] (\text{BF}_4)_2$, HF-py	JOC 58 2791 (1993)
	NBS or NIS, HF-py / AgF, HF-py	Syn 780 (1973)
Cl	Cl ₂	JACS 61 940 (1939); 63 2541 (1941); 73 3329 (1951)
	Cl ₂ , AlCl ₃ , hv	TL 36 3906 (1995)
	CuCl ₂	JOC 36 3324 (1971)
	SO ₂ Cl ₂	JACS 61 940, 3432 (1939)
	PCl ₅	JACS 61 940 (1939)
	NCS, HCl	JACS 81 2191 (1959)
	HCl, CaCl ₂ , H ₂ O ₂ , (PhCH ₂ NEt ₃)Cl	Syn 676 (1977)
	(polymer-C ₆ H ₄ CH ₂ NMe ₃)Cl ₂	CC 1278 (1980)
	(PhCH ₂ NEt ₃)MnO ₄ , ClCOCOCl	SL 733 (1991)
		TL 32 1831 (1991)
Br	Cl ₃ CCCl ₃ , cat RuCl ₂ (PPh ₃) ₃	TL 35 737 (1994)
	Br ₂	Org Syn Coll Vol 1 521 (1941); 2 171, 177, 270 (1943); 4 195 (1963)
		JOC 57 6640 (1992); 60 6214 (1995)
	Br ₂ -dioxane	Zh Obshch Khim 24 610 (1954)
	(C ₅ H ₅ NH)Br ₃	Ber 56 1262 (1923)
		J Chem Ed 31 291 (1954)
		Syn 966 (1979) (selective diene addition)
		TL 22 623 (1981)
		JOC 55 1506 (1990)
	(PhNMe ₃)Br ₃	TL 32 3217 (1991)
	(n-Bu ₄ N)Br ₃ , (ultrasound)	TL 32 4135 (1991)
		JOC 60 6214 (1995)
	(polymer-C ₆ H ₄ CH ₂ NMe ₃)Br ₃	Syn 143 (1980)
	HBr, CaBr ₂ , H ₂ O ₂ , (PhCH ₂ NEt ₃)Cl	Syn 676 (1977)
	NaBr, H ₂ O, H ₂ SO ₄ , CH ₃ CN, electrolysis	JOC 46 3312 (1981)
I	NaBr, NaOCl, (n-Bu ₄ N)HSO ₄	JOC 57 4555 (1992)
	KBr, H ₂ O ₂ , cat NH ₄ VO ₃ , H ₂ O, HCCl ₃	TL 35 7429 (1994)
	BrCCl ₂ CCl ₂ Br, hv	JACS 114 5018 (1992)
	CuBr ₂	JOC 36 3324 (1971)
	I ₂	JACS 115 3071 (1993)
	I ₂ , Al ₂ O ₃	JACS 115 3071 (1993)
	I ₂ , CuO-HBF ₄ , NaI	CC 1491 (1987)



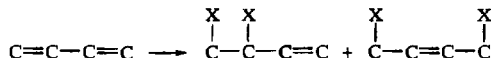
See page 741, Section 12.



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	Cl	 , HF	Bull Acad Sci USSR, Div Chem Sci 1016 (1966)
			JOC USSR 5 1879 (1969); 7 1382, 1876 (1971); 8 1139 (1972)
		NCS, HF-Et ₃ N	Syn 562 (1987)
		NCS, HF-py	Syn 780 (1973)
			JOC 44 3872 (1979); 49 333 (1984)
		NCS, (<i>n</i> -Bu ₄ N)HF ₂	JOC 54 4294 (1989)
		XeF ₂ , R ₃ COCl	TL 33 6903 (1992)
		(CF ₃ SO ₂)NF, HCl	JOC 57 629 (1992)
		<i>N</i> -chlorosaccharin, HF-py	SL 327 (1995)
		review	Russ Chem Rev 41 740 (1972)
		BrF	JOC 50 3342 (1985)
		Br ₂ , AgNO ₃ , HF-py	Syn 780 (1973)
			JOC 44 3872 (1979)
		XeF ₂ , Br ₂	Israel J Chem 10 271 (1977)
		AcNHBr, HF	JACS 81 2191, 4107 (1959); 82 4001 (1960)
	Cl, Br, I Br		Chem Ind 452 (1963)
			JOC 29 1202 (1964)
			Can J Chem 43 1689 (1965)
			Syn 217 (1978)
		AcNHBr, HF-py	JOC 54 3091 (1989)
		NBS, HF	TL 28 4003 (1987)
			JACS 112 363 (1990)
		NBS, HF-Et ₃ N	TL 27 4449 (1986); 30 3167 (1989)
			Syn 562 (1987)
			JOC 59 5277 (1994); 60 6214 (1995)
		NBS, HF-py	Syn 780 (1973)
			JOC 44 3872 (1979); 49 333 (1984)
			J Fluorine Chem 45 377 (1989)
			TL 27 4449 (1986)
			SL 267 (1990)
		NBS, HF, R ₃ N	JOC 54 4294 (1989)
		NBS, polyvinylpyridinium (HF) _n	TL 31 3167 (1990)
		NBS, (<i>n</i> -Bu ₄ N)HF ₂	Can J Chem 43 1689 (1965)
		NBS, (NH ₄)HF ₂ -AlF ₃	J Fluorine Chem 31 99 (1986)
		1,3-dibromo-5,5-dimethylhydantoin, HF	JOC 52 658 (1987)
			TL 28 4003 (1987)
		1,3-dibromo-5,5-dimethylhydantoin, (<i>n</i> -Bu ₄ N)H ₂ F ₃	TL 32 1215 (1991)
		1,3-dibromo-5,5-dimethylhydantoin, pyridinium poly(hydrogen fluoride)	TL 33 7003 (1992)
		1-bromo-3,5,5-trimethylhydantoin, HF	Can J Chem 43 1689 (1965)



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F (continued)	I	IF	JOC 50 3342 (1985)
		I ₂ , AgNO ₃ , HF-py	Syn 780 (1973)
			JOC 44 3872 (1979)
		I ₂ , HF-py	Syn 780 (1973)
		I(py) ₂ BF ₄ , HBF ₄	Angew 24 319 (1985)
			JOC 56 2234 (1991); 59 8034 (1994)
		I(collidine) ₂ BF ₄	Syn 551 (1987)
		NIS, HF	JACS 82 4001, 4007 (1960)
		NIS, HF-Et ₃ N	Syn 562 (1987)
		NIS, HF-py	Syn 780 (1973)
			JOC 44 3872 (1979)
			TL 33 7003 (1992)
Cl	Br	NIS, HF, KHF ₂ , cat <i>n</i> -Bu ₄ NF·3H ₂ O	SL 185 (1991)
		NIS, (NH ₄)HF ₂ ·AlF ₃	TL 31 3167 (1990)
		NIS, (<i>n</i> -Bu ₄ N)HF ₂	JOC 54 4294 (1989)
	I	NIS, (<i>n</i> -Bu ₄ N)H ₂ F ₃	TL 32 1215 (1991); 36 6123 (1995)
		Br ₂ , CuCl ₂	JOC 36 3324 (1971)
		Br ₂ , <i>n</i> -Bu ₄ NCl	JOC 60 6214 (1995)
		AcNHBr, LiCl, HCl	JACS 81 2191 (1959)
Br	I	ICl	JCS Perkin I 226 (1977)
			CC 1577 (1987)
		I ₂ , CuCl ₂	JOC 36 3324 (1971)
		I(py) ₂ BF ₄ , Cl ⁻	Angew Int 24 319 (1985)
		(PhCH ₂ NMe ₃)ICl ₂	BCSI 63 3033 (1990)
		I(py) ₂ BF ₄ , Br ⁻	Angew Int 24 319 (1985)



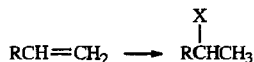
Review: Russ Chem Rev 60 39 (1991)

<u>X</u>	<u>Reagent</u>	
Cl	Cl ₂	JACS 52 4043 (1930); 73 244 (1951)
		JCS 829 (1934); 3204 (1962)
		J Gen Chem USSR 27 253 (1957)
		JOC 31 4167 (1966); 33 2946 (1968); 37 2228 (1972); 39 736 (1974); 41 334 (1976)
		JOC 36 3324 (1971)
	CuCl ₂ ; cat CuCl, CuI or I ₂	TL 35 737 (1994)
	Cl ₃ CCl ₃ , cat RuCl ₂ (PPh ₃) ₃	
Br	Br ₂	Helv 5 756 (1922)
		JCS 729 (1928)
		JACS 75 2512 (1953); 81 5943 (1959)

J Gen Chem USSR 24 453 (1954)
JOC 33 2342 (1968); 34 2779 (1969); 35 2967
 (1970); 37 2228 (1972); 38 4109 (1973)

2. Hydrohalogenation

2.1. Markovnikov Addition



Reviews:

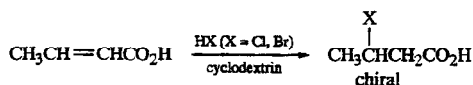
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol V/3, pp 99–108 (X = F) and pp 812–822 (X = Cl); Vol V/4, pp 102–124 (X = Br); and pp 535–539 (X = I), G. Thieme, Stuttgart (1962 and 1960, respectively)
- P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," Elsevier, New York (1966), Chpt 5
- C. A. Buehler and D. E. Pearson, "Survey of Organic Chemistry," Wiley Interscience, New York (1970), Vol 1, p 356
- H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York (1972), pp 446–452
- "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Part 1.7, p 269

<u>X</u>	<u>Reagent(s)</u>	
F	HF	<i>JACS</i> 66 1759 (1944)
	py·(HF) _n	<i>Syn</i> 779 (1973)
		<i>JOC</i> 44 3872 (1979)
	polyvinylpyridinium poly-(hydrogen fluoride)	<i>SL</i> 267 (1990)
Cl	HCl	<i>Org Syn Coll Vol</i> 2 336 (1943)
		<i>JOC</i> 51 5191 (1986)
	HCl, SO ₂	<i>JOC</i> 53 3647 (1988)
	HCl, SiO ₂	<i>JACS</i> 112 7433 (1990); 115 3071 (1993)
	HCl, Al ₂ O ₃	<i>JACS</i> 112 7433 (1990); 115 3071 (1993)
	(COCl) ₂ , SiO ₂	<i>JACS</i> 115 3071 (1993)
	(COCl) ₂ , Al ₂ O ₃	<i>JACS</i> 112 7433 (1990)
	SOCl ₂ , SiO ₂	<i>JACS</i> 112 7433 (1990); 115 3071 (1993)
	SOCl ₂ , various catalysts	<i>TL</i> 32 3705 (1991)
	Me ₃ SiCl, Al ₂ O ₃	<i>JACS</i> 115 3071 (1993)
Br	TiCl ₄ , ROH	<i>JOC</i> 58 7296 (1993)
	HBr	<i>JACS</i> 68 1805 (1946)
		<i>Org Syn Coll Vol</i> 3 576 (1955)
		<i>JOC</i> 21 1362 (1956)
	HBr, SiO ₂	<i>JACS</i> 112 7433 (1990); 115 3071 (1993)
	HBr, Al ₂ O ₃	<i>JACS</i> 115 3071 (1993)
	(COBr) ₂ , SiO ₂	<i>JACS</i> 115 3071 (1993)

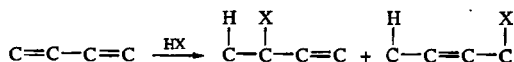
<u>X</u>	<u>Reagent(s)</u>	
Br (<i>continued</i>)	(COBr) ₂ , Al ₂ O ₃	JACS 112 7433 (1990)
	Me ₃ SiBr, SiO ₂	JACS 115 3071 (1993)
	Me ₃ SiBr, Al ₂ O ₃	JACS 115 3071 (1993)
I	KI, H ₃ PO ₄	Org Syn Coll Vol 4 543 (1963)
	I ₂ , Al ₂ O ₃	TL 28 4497 (1987)
		JOC 53 4477 (1988)
	PI ₃ , SiO ₂	JACS 112 7433 (1990); 115 3071 (1993)
	PI ₃ , Al ₂ O ₃	JACS 112 7433 (1990); 115 3071 (1993)
	PhNET ₂ -BI ₃ , HOAc	TL 31 1919 (1990)
	Me ₃ SiI, SiO ₂	JACS 115 3071 (1993)
	Me ₃ SiI, Al ₂ O ₃	JACS 115 3071 (1993)
Cl, Br, I	aq HX (X = Cl, Br, I) (phase transfer)	JOC 45 3527 (1980)



JACS 58 1806 (1936)



JOC 55 564 (1990)

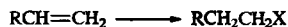


Reviews:

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Part 1.7, p 269
 Russ Chem Rev 60 39 (1991)

<u>X</u>	
Cl	JACS 56 1239 (1934); 63 3474 (1941); 82 6397 (1960); 95 6752 (1973); 101 1288 (1979) JCS 79 (1934); 530 (1948) JOC 2 489 (1937); 56 595 (1991) J Prakt Chem 151 307 (1938) Org Syn Coll Vol 4 238 (1963)
Br	Ber 44 2974 (1911) J Prakt Chem 105 65 (1922-23); 151 307 (1938) Helv 5 750 (1922); 30 1599 (1947) JCS 129 (1931); 261 (1936) JOC 1 393 (1936) JACS 83 2554 (1961)
I	J Prakt Chem 151 307 (1938)

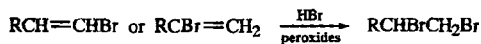
2.2. Anti-Markovnikov Addition



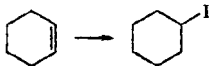
X	Reagents	
Cl	BH ₃ or 9-BBN/Cl ₂ NTs	J Chem Res (S) 376 (1981) JOC 53 5664 (1988)
	BH ₃ /t-BuOCl, NaOAc	JOC 53 5664 (1988)
	BH ₃ /CuCl ₂ , H ₂ O	JOMC 31 421 (1971) BCSJ 47 2511 (1974) JOC 53 5664 (1988)
	BH ₃ /FeCl ₃ , H ₂ O	BCSJ 47 2511 (1974) JOC 53 5664 (1988)
	BH ₃ /NCl ₃	JOMC 135 C57 (1977) JOC 53 5664 (1988)
Br	HBr, peroxides	JOC 11 281 (1946); 47 5372 (1982) IACS 68 1101 (1946); 109 6937 (1987) Chem Rev 62 599 (1962) (review) Org Rxs 13 150 (1963) (review)
	HBr, hv	JOC 21 1362 (1956); 42 1709 (1977) Org Rxs 13 150 (1963) (review) Tetr 25 5149 (1969)
	BH ₃ /Br ₂	JACS 92 7212 (1970) JOC 46 3113 (1981)
	BH ₃ /BrCl	JOC 46 3113 (1981)
	BH ₃ /Br ₂ , NaOCH ₃	JACS 92 6660 (1970) JOC 51 5291 (1986)
	BH ₃ /Hg(OAc) ₂ /Br ₂	JACS 92 3221 (1970)
	BH ₃ /NaBr, chloramine T	JOC 46 3113 (1981)
	BH ₃ /CuBr ₂ , H ₂ O	JOMC 31 421 (1971) BCSJ 47 2511 (1974)
	9-BBN/Br ₂	JOMC 26 C51 (1971)
	i-Bu ₃ Al, cat Cp ₂ ZrCl ₂ /NBS	TL 28 5793 (1987) JACS 110 5383 (1988)
	LiAlH ₄ , Cp ₂ TiCl ₂ /Br ₂	CL 1117 (1977)
	HSiCl ₃ , cat (π-C ₃ H ₅ PdCl) ₂ , cat chiral ligand / KF / NBS (chiral)	TL 33 7185 (1992)
Cl, Br	LiAlH ₄ , TiCl ₄ /CuX ₂	CL 833 (1978)
	LiAlH ₄ , TiCl ₄ or ZrCl ₄ /X ₂	JOMC 142 71 (1977)
	HSiCl ₃ , cat H ₂ PtCl ₆ /KF/CuX ₂	TL 1809 (1978) Organomet 1 369 (1982)
Cl, Br, I	HSiCl ₃ , cat H ₂ PtCl ₆ /KF/X ₂ or NBS	JACS 100 290 (1978) Organomet 1 355 (1982)
	Cp ₂ ZrHCl/PhICl ₂ , Br ₂ or I ₂	JACS 96 8115 (1974)
Br, I	Cl ₂ AlH, cat Et ₃ B/X ₂ , py	JACS 108 6036 (1986)
I	BH ₃ /I ₂ , NaOH	Tetr 44 2751 (1988)
	BH ₃ /I ₂ , NaOCH ₃	JACS 98 1290 (1976) Syn 114 (1976)
		Tetr 44 2751 (1988)

**X****Reagents****I (continued)**

BH_3/ICl , NaOAc	JOC 45 3578 (1980)
BH_3/NaI , chloramine T	JOC 46 2582 (1981); 52 28 (1987)
$(\text{Sia})_2\text{BH}/\text{I}_2$, NaOH	JACS 90 5038 (1968)
	Tetr 44 2751 (1988)
	SL 57 (1992)
$\text{Cy}_2\text{BH}/\text{I}_2$, NaOCH ₃	JACS 107 3915 (1985)
$\text{Cy}_2\text{BH}/\text{ICl}$, NaOAc	Syn Commun 11 521 (1981)
	JACS 117 3705 (1995)
NaBH_4 , $\text{Hg}(\text{OAc})_2/\text{I}_2$, NaOH	JOC 53 187 (1988)
$i\text{-Bu}_3\text{Al}$, cat $\text{Cp}_2\text{ZrCl}_2/\text{I}_2$	TL 21 1501 (1980)
$\text{Cp}_2\text{ZrHCl}/\text{I}_2$	JACS 110 2506 (1988)
	SL 285 (1992)
Et_2Zn , cat $\text{Ni}(\text{acac})_2$, cat COD / $\text{CuCN} \cdot 2\text{LiCl}/\text{I}_2$	TL 36 1023 (1995)



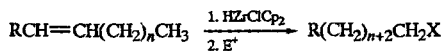
JACS 58 1806 (1936)

2.3. Unknown Regiochemistry I_2 , $\text{CuO} \cdot \text{HBF}_4$, Et_3SiH

CC 1491 (1987)

 $\text{I}(\text{py})_2\text{BF}_4$, Et_3SiH

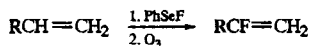
Angew 24 319 (1985)

2.4. Isomerization—Addition $\text{E}^+ = \text{NCS}$, PhICl_2 , NBS , Br_2 , I_2 ; $\text{X} = \text{Cl}$, Br , I

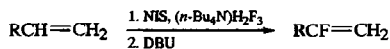
JACS 96 8115 (1974); 98 262 (1976)

Angew Int 15 333 (1976)

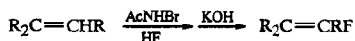
JOC 46 1821 (1981)

3. Hydrogen Substitution

TL 31 973 (1990)



TL 32 1215 (1991)



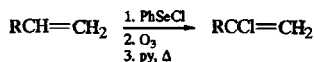
Syn 217 (1978)



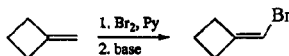
JOC 52 4086 (1987)



TL 28 1463 (1987)

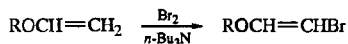


JACS 109 7543 (1987)

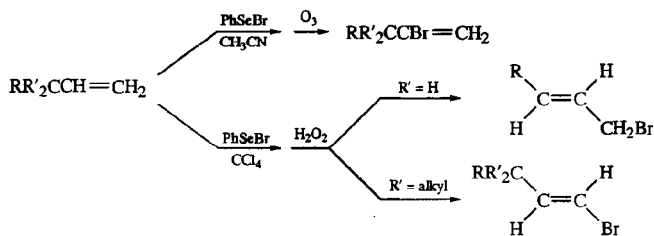


JOC 30 2208 (1965); 36 1031 (1971)

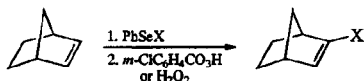
JACS 111 1429 (1989)



JOC 58 5690 (1993)



TL 3909 (1977)



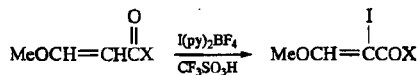
X = Cl, Br

TL 30 7415 (1989); 34 1017 (1993); 35 111 (1994)

JOC 54 2628 (1989)

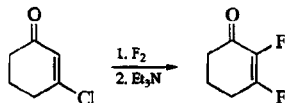


<u>X</u>	<u>Reagent(s)</u>	
Cl, Br	PhSeX, py	TL 22 3301 (1981)
Br	Br ₂ /NaHCO ₃	Syn 389 (1982)
	Br ₂ /Et ₃ N	JOC 33 1454 (1968); 58 2714 (1993); 59 2910 (1994)
		TL 28 6485 (1987)
		JACS 110 4741 (1988); I12 8465 (1990)
		Org Syn Coll Vol 7 271 (1990)
I	I ₂ , py	TL 33 917 (1992); 34 7641 (1993)
	I ₂ , PDC	TL 35 6787 (1994)
	IN ₃	Can J Chem 49 3045 (1971)
		TL 34 7641 (1993)
	Me ₃ SiN ₃ /I ₂ , py	TL 36 6927 (1995)

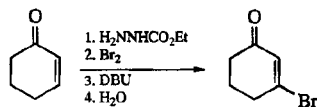


X = Me, OMe

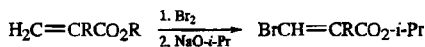
TL 36 5257 (1995)



TL 36 6705 (1995)



TL 34 2103 (1993)



JOC 50 2195 (1985)

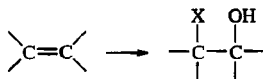
4. Halofunctionalization

Reviews:

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 3.7, p 527



Syn 1177 (1993)

For the synthesis of vinylic halides via halofunctionalization of alkynes, see page 655, Section 4.

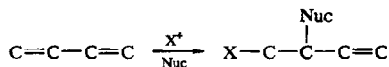


Review: Russ Chem Rev 41 740 (1972)

X
Reagents

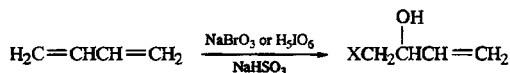
F	(CF ₃ SO ₂)NF, H ₂ O	JOC 57 629 (1992)
	[HON  NF](BF ₄) ₂ , H ₂ O	TL 36 6769 (1995)
	[ClCH ₂ N  NF](BF ₄) ₂ , H ₂ O	JOC 58 2791 (1993) (styrenes)
Cl	Cl ₂ , H ₂ O	JCS 119 1774 (1921); 121 2595 (1922); 1817 (1949) Ber 61 510, 518 (1928) JACS 72 4608 (1950) Org Syn 33 15 (1953) Ann 596 140 (1955) Ann 596 138 (1955) Org Syn Coll Vol 1 158 (1941) JCS 1817 (1949) Helv 35 1263 (1952); 39 423 (1956) Ber 89 2424 (1956) JACS 79 2341 (1957) Rec Trav Chim 50 261 (1931) Ber 58 572 (1925) JCS 114 (1946); 239 (1949) Helv 35 1263 (1952) JACS 63 2541 (1941) JCS 1817 (1949) JACS 44 148 (1922) JACS 58 2396 (1936) JACS 67 516 (1945); 71 2666 (1949) BSCF 1240 (1964) Syn Commun 9 37 (1979) TL 30 3175 (1989) JOC 50 912 (1985) JOC 58 6944 (1993) JOC 60 6214 (1995) BSCF 31 102, 169, 176 (1922) Org Syn Coll Vol 4 157 (1963) Syn 362 (1981)
	Cl ₂ , H ₂ O, HgCl ₂	
	Cl ₂ , H ₂ O, HgCl ₂ , NaOH/HNO ₃	
	Cl ₂ , H ₂ O, NaHCO ₃ , CO ₂	
	HOCl, H ₂ O	
	HOCl, H ₂ O, CuCl ₂	
	EtOCl/H ₂ O	
	<i>t</i> -BuOCl, H ₂ O, HOAc	
	<i>t</i> -BuOCl, HOAc	
	<i>t</i> -BuOCl, HOAc, H ₂ SO ₄	
	NaOCl, H ₂ O, CO ₂	
	KOCl, H ₂ O, CO ₂	
	Ca(OCl) ₂ , HOAc, H ₂ O	
	Ca(OCl) ₂ , CO ₂ , H ₂ O	
	Me ₃ SiCl, H ₂ O ₂	
	PhSeCl, H ₂ O	
	TiCl ₄ , <i>t</i> -BuO ₂ H or (<i>t</i> -BuO) ₂	
	CuCl ₂ , cat PdCl ₂ , H ₂ O	
	NCS, H ₂ O	
	CINHCONH ₂ , H ₂ O	
	CINHCONH ₂ , HOAc, H ₂ O	
	TsNCINa, H ₂ O	
Br	Br ₂ , H ₂ O	Ann 348 285 (1906) JCS 111 240 (1917); 117 359 (1920); 119 1774 (1921) J Biol Chem 178 709 (1949) JCS 101 758 (1912); 1487 (1928) JOC 18 1586 (1953)
	Br ₂ , H ₂ O, KBr	

<u>X</u>	<u>Reagents</u>	
Br (continued)	Br ₂ , H ₂ O, Na ₂ CO ₃	Ber 54 1945 (1921)
	Br ₂ , H ₂ O, NaHCO ₃ , CO ₂	JCS 1817 (1949)
	Br ₂ , H ₂ O, HgO	Helv 7 108 (1924)
		JCS 285 (1936); 1817 (1949)
	HOBBr, H ₂ O	Helv 35 1263 (1952)
		JACS 79 2341 (1957)
	NaBrO ₃ , NaHSO ₃	JOC 59 5550 (1994)
	Ca(OBr) ₂ , H ₃ BO ₃	Ber 32 3490 (1899)
	CH ₃ CONHBr, H ₂ O	Ber 59 1279 (1926)
		JACS 64 2780 (1942); 74 1160 (1952); 78 1740 (1956)
		Helv 26 562, 586, 705, 721, 1799 (1943)
		Gazz Chim Ital 108 643 (1978)
		JOC 52 4384 (1987); 54 1459 (1989)
	CH ₃ CONHBr, H ₂ O, H ⁺	JACS 61 1576 (1939); 79 1130 (1957)
		JOC 18 1586 (1953); 51 3407 (1986)
	CH ₃ CONHBr, H ₂ O, HOAc, NaOAc	Helv 27 821 (1944); 28 1420 (1945); 30 1616 (1947)
	NBS, H ₂ O	JACS 74 1160 (1952); 76 4373 (1954); 77 2549 (1955)
		Can J Chem 43 2398 (1965)
		JOC 35 2670 (1970); 60 6214 (1995)
		TL 33 1475 (1992); 35 6997 (1994)
	NBS, H ₂ O, DMSO	JACS 90 5498 (1968)
		Org Syn Coll Vol 6 184 (1988)
	NBS, H ₂ O, H ⁺	JCS 401 (1952)
		JACS 76 5017 (1954)
	I ₂ , H ₂ O	Ber 58 794, 1064, 1071 (1925); 59 113, 375 (1926); 60 991 (1927)
		JCS C 928 (1970)
	I ₂ , H ₂ O, sulfolane, HCCl ₃	JCS Perkin I 226 (1977)
	I ₂ , H ₂ O / H ₂ O ₂	Can J Chem 42 2710 (1964)
	I ₂ , H ₂ O, HgO	Compt Rend 130 1766 (1900); 131 528 (1900); 135 1055 (1902)
		BSCF 5 115 (1909)
		JCS 1817 (1949)
	I ₂ , H ₂ O, CuO-HBF ₄	CC 1491 (1987)
	I ₂ , H ₂ O, NaNO ₂ , H ⁺	JCS C 846 (1970)
	I ₂ , H ₂ O, KIO ₃ , H ⁺	JCS C 846 (1970)
	I ₂ , H ₂ O, Ag ₂ O	JOC 59 4316 (1994)
	I ₂ , AgO ₂ CCF ₃ / MeOH	TL 27 4245 (1986)
	I ₂ , PDC, molecular sieves	Tetr 39 1765 (1983)
	I(py) ₂ BF ₄ , H ₂ O	Angew Int 24 319 (1985)
	NIS, H ₂ O	TL 35 1405 (1994)
		JOC 60 6214 (1995)
	NIS, NaHCO ₃ , H ₂ O	TL 36 2195 (1995)
	NCS, NaI, NaHCO ₃ , H ₂ O	TL 36 2195 (1995)
	H ₅ IO ₆ , NaHSO ₃	JOC 59 5550 (1994)



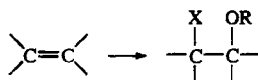
Nuc = H₂O, ROH, RCO₂H

Review: Russ Chem Rev 60 39 (1991)



X = Br, I

JOC 59 5550 (1994)



For intramolecular reactions, see page 889, Section 2.

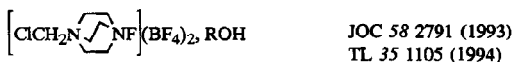
Review: Russ Chem Rev 41 740 (1972)

X

Reagents

F

CsSO ₄ F, ROH	JOC 52 919 (1987)
XeF ₂ , CH ₃ OH	JOC 50 2751 (1985)
XeF ₂ , ROH, cat BF ₃ ·OEt ₂ or HF	JCS Perkin II 159 (1989)
MeOF	JOC 59 4281 (1994)
CF ₃ OF (R = CF ₃)	CC 227 (1969)
<i>t</i> -BuOF (R = <i>t</i> -Bu)	JCS Perkin I 739 (1974)
FCIO ₃ , ROH	JACS 115 1379 (1993)
CH ₃ OH, Hg(OAc) ₂ /NaCl/CH ₃ CO ₂ F	JOC 52 978 (1987)
	JOC 52 2588 (1987)



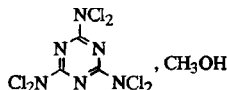
Cl

Cl ₂ , ROH	JACS 48 2166 (1926)
<i>t</i> -BuOCl, ROH	JACS 63 858, 1624 (1941); 72 4608 (1950); 73 2302 (1951)
	Chem Rev 54 925 (1954) (review)
PhSO ₂ NCl ₂ , ROH	J Gen Chem USSR 8 370 (1938)
	[CA 32 519 (1938)]
	JACS 76 693 (1954)

X

Reagents

Cl (continued)



JOC USSR 5 1879 (1969); 7 1876 (1971)

Br

Br₂, ROH

JACS 46 1727 (1924); 48 2166 (1926); 71 1096 (1949); 74 5518 (1952); 114 7773 (1992)

Helv 35 762 (1952)

JOC 53 2199, 5909 (1988); 60 6214 (1995)

TL 36 3251 (1995)

Ann 516 231 (1935)

J Biol Chem 122 605 (1938)

JOC 53 2199 (1988)

Ber 59 1279 (1926)

JACS 65 2196 (1943); 74 1160 (1952)

JOC 17 233 (1952)

JACS 76 4368, 4373 (1954); 110 531 (1988); 114 7773 (1992)

TL 28 2009 (1987)

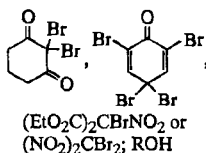
JOC 53 3912 (1988)

JACS 69 2001 (1947); 76 693 (1954)

Ber 55 2099 (1922); 56 1239 (1923); 57 2039 (1924); 59 1279, 1876 (1926)

Br₂, ROH, AgNO₃Br₂, NBS, ROHCH₃CONHBr, ROH

NBS, ROH

PhSO₂NBr₂, ROHBrC(NO₂)₃, ROH

Ber 59 1876 (1926)

I

ICl, ROH

JACS 50 2249 (1928)

I₂, MeOH

JCS Perkin I 226 (1977)

I₂, MeOH, AgNO₃

JOC 59 1166 (1994)

I₂, MeOH, HgO

Compt Rend 135 1055 (1902)

BSCF 1 1212 (1907); 13 354 (1913); 15 175, 182 (1914)

I₂, ROH, Cu(OAc)₂·H₂O

Syn 402 (1978)

I₂, ROH / Cl₂

JACS 50 2249 (1928)

NIS, ROH

JACS 109 8119 (1987)

I(py)₂BF₄, ROH

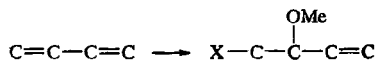
Angew Int 24 319 (1985)

[I(sym-collidine)₂]ClO₄, ROH

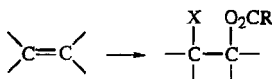
JACS 111 6656 (1989); 112 8895 (1990); 113 5080 (1991); 114 3471, 4518 (1992)

t-BuOI, hv or BF₃·OEt₂

JOC 53 198 (1988)



<u>X</u>	<u>Reagents</u>	
Br	Br ₂ , MeOH	JOC 35 539 (1970)
I	I ₂ , CuO·HBF ₄ , MeOH	CC 1491 (1987)
	I(py) ₂ BF ₄ , MeOH	TL 27 1715 (1986)



For halolactonization, see page 1861, Section 8.

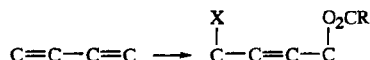
<u>X</u>	<u>Reagent(s)</u>	
F	CH ₃ CO ₂ F	CC 443 (1981)
	CF ₃ CO ₂ F	JOC 45 672 (1980)
	n-C ₇ F ₁₅ CO ₂ F	JOC 50 3698 (1985)
	$ \left[\begin{array}{c} \text{Cl} \quad \text{Cl} \\ \quad \\ \text{Cl} \quad \text{NF} \\ \quad \\ \text{Cl} \quad \text{Cl} \end{array} \right] \text{OTf, RCO}_2\text{H} $	JACS 112 8563 (1990)
	$ \begin{array}{c} \text{SO}_3^- \\ \\ \text{CF}_3-\text{C}_6\text{H}_3-\text{NF}^+ \\ \\ \text{CF}_3 \end{array} \text{RCO}_2\text{H} $	JOC 60 6563 (1995)
	$ \left[\text{HON} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{NF} \right] (\text{BF}_4)_2, \text{RCO}_2\text{H} $	TL 36 6769 (1995)
	$ \left[\text{ClCH}_2\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{NF} \right] (\text{BF}_4)_2, \text{RCO}_2\text{H} $	JOC 58 2791 (1993)
	(CF ₃ SO ₂)NF, RCO ₂ H	JOC 57 629 (1992)
Cl	Cl ₂ , RCO ₂ H	JACS 61 1457 (1939)
	Cl ₂ , Ac ₂ O, NaOAc	J Gen Chem USSR 25 709 (1955)
	Cl ₂ , AgO ₂ CR	JACS 61 1457 (1939)
	NCS, CF ₃ CO ₂ H	Ber 68 824 (1935)
	t-BuOCl, RCO ₂ H	JOC 45 154 (1980)
	CrO ₂ Cl ₂ , AcCl	JACS 63 858 (1941)
	AcOCl	TL 3523 (1977)
	TsNCINa·3H ₂ O, RCO ₂ H	Ann 519 165 (1935)
		TL 21 1709 (1980)
Br	Br ₂ /NaOAc	JACS 76 693 (1954)
	Br ₂ , AgO ₂ CR	Ber 68 824 (1935)
	Br ₂ , Hg(OAc) ₂ , HOAc	JCS 1515, 2934 (1952); 762 (1954)
	RCO ₂ Br	J Gen Chem USSR 25 709 (1955)
	CH ₃ CONHBr, HCO ₂ H	Ann 519 165 (1935)
	CH ₃ CONHBr, HOAc, LiOAc	Ber 59 1279 (1926)
	2,4,6-Br ₃ C ₆ H ₂ NBrCOCH ₃ , RCO ₂ H, py	TL 27 4253 (1986); 30 123 (1989)
	NBS, NaOAc, HOAc	JCS 762 (1954)
	NBS, CF ₃ CO ₂ H	JOC 53 3912 (1988)
	NBS, Ph ₂ CHCO ₂ H	JOC 45 154 (1980)
		SL 347 (1992)

<u>X</u>	<u>Reagent(s)</u>	
Br (<i>continued</i>)	BrC(NO ₂) ₃ , HCO ₂ H	Ber 56 1239 (1923)
I	ICl, TiO ₂ CR	JCS Perkin I 226 (1977)
	I ₂ , NaO ₂ CR	JCS Perkin I 226 (1977)
	I ₂ , KOAc, Al ₂ O ₃	CC 1301 (1987)
	I ₂ , TiO ₂ CR	CC 359 (1973)
		JCS Perkin I 1858 (1974); 1157 (1977)
	I ₂ , AgO ₂ CR	Ber 65 1339 (1932); 67 1729 (1934)
		JCS Perkin I 1157 (1977)
		JACS 111 278 (1988)
	I ₂ , KIO ₃ , RCO ₂ H	Gazz Chim Ital 104 835 (1974)
	I(py) ₂ BF ₄ , RCO ₂ H	Angew Int 24 319 (1985)
	NIS, RCO ₂ H	TL 3661 (1976); 29 1085 (1988)

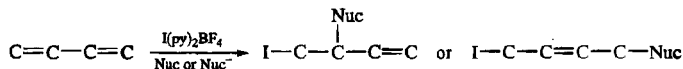


RCO₂X (X = Cl, Br) JOC 37 2228 (1972)

t-BuOCl, HCO₂H Ann 1015 (1987)

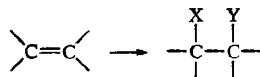


<u>X</u>	<u>Reagents</u>	
Cl	cat Pd(OAc) ₂ , LiCl, LiOAc·2H ₂ O, benzoquinone, HOAc	TL 23 1617 (1982); 28 4199 (1987); 29 191 (1988) Tetr 41 5761 (1985) JACS 107 3676 (1985) JOC 54 3374 (1989); 55 826 (1990); 56 2769 (1991) Org Syn Coll Vol 8 5, 9 (1993) TL 34 6021 (1993)
	<i>t</i> -BuOCl, HCO ₂ H	TL 34 6021 (1993)
I	I ₂ , HOAc, CuO·HBF ₄	CC 1491 (1987)



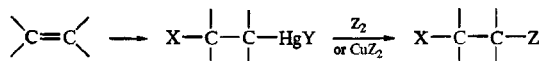
Nuc = H, Cl, OMe, O₂CH, NO₂, NHCOCH₃, Ar

TL 27 1715 (1986); 29 6497 (1988)



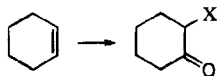
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	NO ₂	(NO ₂)BF ₄ , HF-py	JOC 44 3872 (1979)
	O ₃ SCF ₃	XeF ₂ , CF ₃ SO ₃ H	JOC 56 1416 (1991)
	OSO ₂ F	XeF ₂ , HOSO ₂ F	JOC 56 1416 (1991)
	ONO ₂	XeF ₂ , HNO ₃	JOC 56 1416 (1991)
	SMe	(Me ₂ SSMe)BF ₄ , Et ₃ N, HF	TL 29 2311 (1988) JOC 57 714 (1992)
Cl	SR	RSCl/HF-Et ₃ N	J Fluorine Chem 47 467 (1990)
	SePh	(PhSe) ₂ , XeF ₂	TL 31 3583 (1990)
	NCICOPh	Cl ₂ NCOPh	Chem Pharm Bull 18 281 (1970)
	NCISO ₂ Ph	Cl ₂ NSO ₂ Ph	Chem Pharm Bull 15 1193 (1967); 18 281 (1970)
	N ₃	Cl ₂ , NaN ₃	TL 3309 (1969) Acct Chem Res 4 9 (1971) (review)
Cl, Br	SePh	PhSeCl, ZnCl ₂	TL 36 1929 (1995)
	SR	RSX (X = Cl, Br)	"The Chemistry of the Sulfenic Acids," G. Thieme, Stuttgart (1973), p 2 (review) "Topics in Sulfur Chemistry," G. Thieme, Stuttgart (1977), Vol 3, p 100 (review) "Chemistry of Double-Bonded Functional Groups," Suppl A, Part 2, Ed. S. Patai, Wiley, Chichester (1977), Chpt 9 (review) Acct Chem Res 12 282 (1979) (review)
	NBrSO ₂ Ar	Br ₂ NSO ₂ Ar	Chem Pharm Bull 15 1193 (1967); 16 1881, 1885, 2267 (1968) JCS Perkin I 1682 (1978) JACS 112 5811 (1990); 113 5863 (1991)
	N ₃	Br ₂ , NaN ₃	JACS 90 216 (1968) TL 3309 (1969) Acct Chem Res 4 9 (1971) (review)
		NBS, NaN ₃ NBS, Me ₃ SiN ₃	Angew Int 13 279 (1974) SL 487 (1990)
I	N ₃	ICl, NaN ₃	JACS 87 4203 (1965); 89 2077 (1967) TL 3309 (1969); 35 2039 (1994) Acct Chem Res 4 9 (1971) (review) JOC 51 1985 (1986); 54 4525 (1989); 57 5823 (1992) Carbohydr Res 166 195 (1987) Org Syn Coll Vol 6 893 (1988) CC 1301 (1987)
		I ₂ , NaN ₃ , Al ₂ O ₃	

<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
I (cont'd)	N ₃ (cont'd)	I ₂ , NaN ₃ , Adogen 464, H ₂ O, HCCl ₃	Syn 462 (1977)
		I ₂ , NaN ₃ , sulfolane, HCCl ₃	JCS Perkin I 226 (1977)
	NO ₂	I ₂ , N ₂ O ₄	JACS 80 338 (1958)
			Org Syn Coll Vol 6 799 (1988)
		I ₂ , CuO, HBF ₄ , NaNO ₂	CC 1491 (1987)
		I(py) ₂ BF ₄ , NO ₂ ⁻	Angew Int 24 319 (1985)
	NCO	I ₂ , AgNCO	Tetr 20 1037 (1964)
			Org Syn Coll Vol 6 795 (1988)
			TL 30 3335 (1989)
		I(py) ₂ BF ₄ , NCO ⁻	Angew Int 24 319 (1985)
	NHCOCH ₃	I(py) ₂ BF ₄ , CH ₃ CN	Angew Int 24 319 (1985)
	NRCO ₂ Et	I ₂ , RNHCO ₂ Et, K ₂ CO ₃	TL 30 2611 (1989)
			(intramolecular)
	NHSO ₂ R	[I(sym-collidine) ₂]ClO ₄ , H ₂ NSO ₂ R	JACS 112 5811 (1990); 114 8331 (1992)
	O ₂ SAr	I ₂ , CuO-HBF ₄ , NaO ₂ SAr	CC 1491 (1987)
	SCN	ICl, KSCN, HCCl ₃ , sulfolane	TL 1531 (1976)
		I ₂ , (SCN) ₂	TL 3567 (1972)
		I ₂ , KSCN, HCCl ₃ , sulfolane	TL 1531 (1976)
		I ₂ , KSCN, 18-crown-6, HCCl ₃	Syn 462 (1977)
		I ₂ , KSCN, Adogen 464, H ₂ O, HCCl ₃	Syn 462 (1977)
		I ₂ , KSCN, Al ₂ O ₃	CC 1301 (1987)
		I ₂ , TiSCN, HCCl ₃ , sulfolane	TL 1531 (1976)
	C ₆ H ₄ OMe	I ₂ , CuO-HBF ₄ , C ₆ H ₅ OMe	CC 1491 (1987)
	Ar	I(py) ₂ BF ₄ , Ar-H	Angew Int 24 319 (1985)



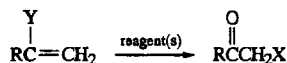
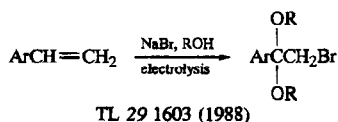
X = HO, RO, RO₂, RCO₂, R₂N, RCONH, N₃, F; Y = OAc, O₂CCF₃, NO₂, F, Cl; Z = Cl, Br, I

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986) (review)



<u>X</u>	<u>Reagent(s)</u>	
F	FeClO ₃	JACS 85 232 (1963)
Cl	O ₂ , FeCl ₃ , py, hν	JOC 46 509 (1981)
	CrO ₂ Cl ₂	Syn Commun 11 7 (1981)
		JOC 58 512 (1993)
	CrO ₃ , Me ₃ SiCl	TL 30 193 (1989)
	2-cyanopyridinium chlorochromate	TL 29 6707 (1988)

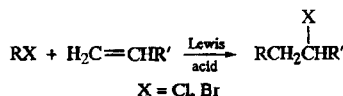
Br	NaBrO ₂ , HOAc, H ₂ O	CL 1481 (1983)
I	I ₂ , PCC	TL 21 4521 (1980)



<u>X</u>	<u>Y</u>	<u>Reagents</u>	
Cl	Cl	NCS, cat HX, H ₂ O	TL 34 4481 (1993)
Br	Cl	NBS, H ₂ O	TL 33 1733 (1993)
	Cl, Br	NBS, cat HX, H ₂ O	TL 34 4481 (1993)
	Br	NBS, H ₂ O	TL 34 4485 (1993)
		Br ₂ , NaHCO ₃ , H ₂ O	TL 34 4485 (1993)
I	Cl	NIS, cat HX, H ₂ O	TL 34 4481 (1993)

5. Haloalkylation

For the formation of lactones and lactams, see page 1861, Section 8.



Review: Angew Int 20 184 (1981)

FX

RX

JACS 67 1152 (1945); 75 6217 (1953)
JOC 48 1159 (1983)

ArCHRX

JOC 29 2685 (1964); 44 3022 (1979); 48 1159
(1983); 50 2995 (1985)
TL 29 6925 (1988)

Me₂C=CHCH₂Cl

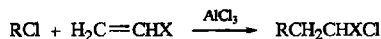
Angew Int 20 1027 (1981); 21 82 (1982)

RCHClOR

Ann 525 151 (1936)
Angew Int 6 335 (1967) (review)
JOC 48 1159 (1983)



TL 28 4517 (1987)



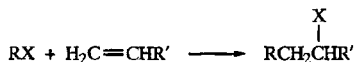
X = Cl, Br

Rec Trav Chim 84 31 (1965)


L. Brandsma, "Preparative Acetylenic Chemistry," Elsevier, Amsterdam (1971), p 189

J Chem Res (S) 106 (1978)

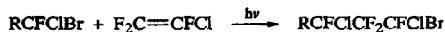
JACS 110 5986 (1988)



Review: Syn 145 (1977)

Reagent(s)	R-X	
hv	Br ₃ C-Br	JACS 69 1100 (1947) JOC 58 3772 (1993)
		TL 34 3087 (1993)
Δ	(NC) ₂ CR-I (R = Me, allylic, propargylic)	JACS 112 9401 (1990); 114 4436 (1992); 115 8585 (1993) TL 32 6307 (1991)
cat AIBN	(RO ₂ C) ₂ CR-Br, NCCHX-Br (X = CO ₂ R, CN)	JOC 54 308 (1989)
cat (AcO) ₂	X ₃ C-X (X = Cl, Br), Br ₂ CH-Br	JACS 69 1100 (1947)
cat (PhCO ₂) ₂	RSO ₂ CHR-I	TL 32 3259 (1991) JACS 117 3272 (1995) SL 866 (1995)
	Cl ₃ C-Cl	J Mol Catal 92 269 (1994)
	Cl ₃ C-Cl, X ₂ CH-X (X = Cl, Br)	JACS 69 1100 (1947)
air, Et ₃ B	XCH ₂ -Br(I) (X = CO ₂ R, CN), (RO ₂ C) ₂ CR-Br	TL 35 2763 (1994)
(n-Bu ₃ Sn) ₂ , hv	(RO ₂ C) ₂ CR-I	JACS 111 8872 (1989)
cat TiO ₂ -Ag or TiO ₂ -Fe ₃ O ₄ , hv	Cl ₃ C-Cl	JOC 59 1279 (1994)
VCl ₂	Cl ₃ C-Br	SL 217 (1990)
cat Mn(OAc) ₂ , electrolysis	(RO ₂ C) ₂ CH-Br	SL 659 (1991)
cat Mn(OAc) ₂ , cat NCCH ₂ CO ₂ Me, KOAc, HOAc, electrolysis	Br ₃ C-Br, Cl ₃ C-Br, BrCF ₂ -Br, MeO ₂ CCHBr-Br	TL 33 213 (1992)
cat FeCl ₃ , H ₂ O	Cl ₃ C-Cl	JCS 1887 (1963)
Fe, CuBr	RO ₂ CCrCl-Br	TL 36 2509 (1995)
cat RuCl ₂ (PPh ₃) ₃	Cl ₃ C-Cl	J Mol Catal 92 269 (1994)
cat Pd(PPh ₃) ₄	RCOCF ₂ -I	TL 34 3239 (1993) JOC 60 5570 (1995)
	(EtO) ₂ POCF ₂ -I	JOC 57 4676 (1992)
Zn, cat NiCl ₂ ·6H ₂ O	RO ₂ CCF ₂ -I	JOC 57 5144 (1992)

Cu	RO ₂ CCF ₂ -I F ₂ C=CF CF ₂ -I	JOC 56 5125 (1991) SL 141 (1992)
cat CuCl, H ₂ NCH ₂ CH ₂ OH	RCXY-Z (X, Y = F, Cl, Br; Z = Cl, Br, I)	TL 5163 (1966) JOC 35 1339 (1970); 53 6150 (1988); 54 3992 (1989); 56 4322 (1991)
cat CuCl(Et ₂ NH) ₂	Cl ₃ C-Cl	J Mol Catal 92 269 (1994)
cat CuCl(<i>i</i> -PrNH ₂) ₂	X ₃ CCl ₂ -Cl (X = H, F)	Coll Czech Chem Commun 57 1291 (1992)
cat CuCl(<i>i</i> -PrNH ₂) ₂ , microwave irradiation	XCCl ₂ -Cl (X = Cl, CO ₂ Et)	TL 33 2039 (1992)
cat CuCl, TMEDA	Cl ₃ C-Cl	JOC 62 1550 (1997)
cat CuCl or CuCl ₂ or CuO or Cu ₂ O; cat Et ₂ NH	Cl ₃ C-Cl	Coll Czech Chem Commun 45 3502 (1980)
cat CuCl ₂ , H ₂ O	Cl ₃ C-Cl	JCS 1887 (1963)
cat CuO, cat Et ₂ NH	Cl ₃ C-Cl	Coll Czech Chem Commun 45 3488, 3502 (1980)



J Fluorine Chem 31 363 (1986)
JOC 59 1844 (1994)



X = COR, CO₂R, CONR₂, CN

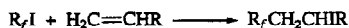
TL 35 1813 (1994)
JOC 60 6798 (1995)



X = halogen

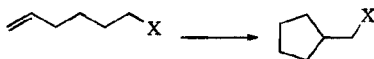
various initiators Syn 145 (1977) (review)

CuCl, hν TL 21 4457 (1980)



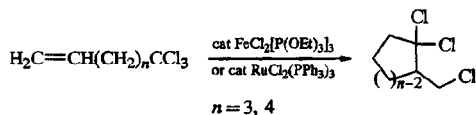
hν	JCS 2856 (1949); 3490 (1952); 1199 (1953) JOC 27 4491 (1962); 44 1964 (1979); 56 5143 (1991); 60 3465 (1995)
Δ	JCS 2856 (1949); 3483 (1952) JOC 27 4491 (1962); 29 1247 (1964); 58 972 (1993); 59 6804 (1994) Bull Acad Sci USSR, Div Chem Sci 359 (1964)

electrolysis	J Fluorine Chem 16 553 (1980)
AIBN	JOC 27 3033, 4491 (1962); 29 1247 (1964); 31 2879 (1966); 44 1964 (1979); 57 132 (1992) J Fluorine Chem 20 313 (1982) TL 30 3243 (1989); 33 2489 (1992)
(<i>t</i> -BuO) ₂	JOC 29 1247 (1964)
(PhCO ₂) ₂	JOC 44 1964 (1979); 47 2251 (1982); 58 419 (1993) J Fluorine Chem 20 313 (1982)
Na ₂ S ₂ O ₄ , ultrasound or phase transfer	TL 31 5615 (1990)
NaO ₂ SR	JOC 50 3269 (1985)
cat Et ₃ B	TL 30 3159 (1989)
cat Mn(OAc) ₂ , cat NCCH ₂ CO ₂ Me, KOAc, HOAc, electrolysis	TL 33 213 (1992)
cat Ru-C, Pt-C, Ag-Al ₂ O ₃ , Ni(CO) ₂ (PPh ₃) ₂ , W(CO) ₅ [P(OEt) ₃] or Mo(CO) ₅ (PPh ₃)	J Fluorine Chem 28 229 (1985)
cat Ru ₃ (CO) ₁₂ , Fe ₃ (CO) ₁₂ , Fe ₂ (CO) ₉ , Fe(CO) ₅ or Co ₂ (CO) ₈ plus cat amine	TL 25 303 (1984) JOC 56 4996 (1991)
cat Raney Ni	CC 498 (1986)
cat Pd(PPh ₃) ₄	Acta Chimica Sinica 43 1118 (1985) CL 1895 (1986) JCS Perkin I 563 (1988) TL 32 1019 (1991) SL 873 (1991) JOC 58 419 (1993)
cat Cu	J Fluorine Chem 28 399 (1985)
cat CuCl, ethanolamine	JOC 35 1339 (1970)

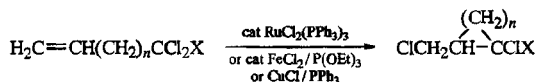


X = Br, I

cat (<i>n</i> -Bu ₃ Sn) ₂ , Δ or hv	TL 27 5821 (1986); 28 2477 (1987); 31 933 (1990) JACS 110 7536 (1988); 113 6607 (1991)
Mg/Cp ₂ TiCl ₂ /EtAlCl ₂ /py/Br ₂	JACS 112 9441 (1990)
cat Pd(PPh ₃) ₄	TL 23 5315 (1982); 26 1519 (1985) Tetr 41 5465 (1985) CC 1375 (1986)
cat Pd(dppe) ₂	TL 31 933 (1990)
Zn/I ₂	TL 34 6053 (1993)

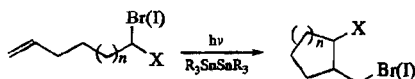


JOC 55 1281 (1990)



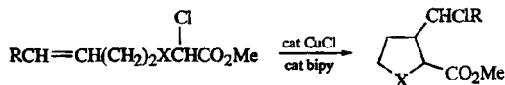
$n = 3, 4$; $\text{X} = \text{CO}_2\text{R}, \text{CN}$

JACS 110 5533 (1988)



$\text{X} = \text{COR}, \text{CO}_2\text{R}, (\text{CO}_2\text{R})_2$; $n = 1, 2$

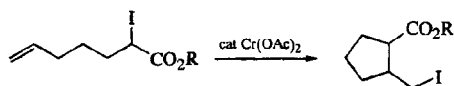
JOC 54 3140 (1989); 57 4883 (1992)



$\text{X} = \text{O}, \text{NCO}_2\text{R}$

TL 32 3123 (1991)

JOC 59 1993 (1994)



SL 861 (1991)



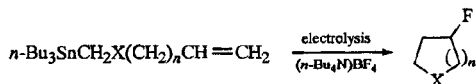
$\text{X} = \text{Br}, \text{I}$

SmI_2/I_2

JACS 114 6050 (1992)

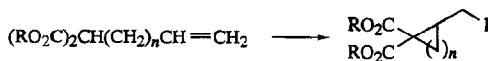
$\text{Co}(\text{salophen})/\text{MeSO}_2\text{Cl}, \text{BrCCl}_3 \text{ or } \text{I}_2$

TL 28 1451 (1987)



$n = 2, 3$; $\text{X} = \text{O}, \text{NCO}_2\text{Me}$

JACS 114 7594 (1994)

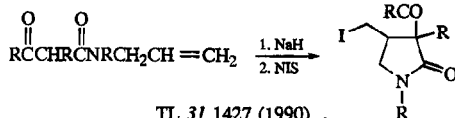
ReagentsNaH/I₂*n*

1, 3, 4

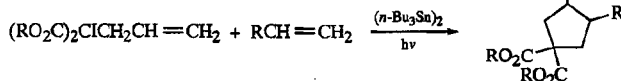
TL 33 4975 (1992)

I₂, Ti(O-*i*-Bu)₄, (CuO)

1, 3

TL 33 2167 (1992); 35 1059 (1994)
JOC 58 3106 (1993)

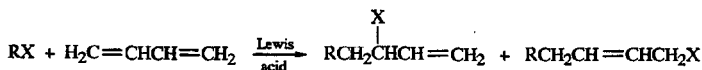
TL 31 1427 (1990)



JACS 111 8872 (1989)

JOC 55 3673 (1990)

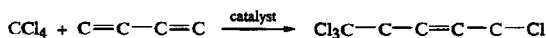
TL 33 7281 (1992)



Angew Int 20 184 (1981)

Ber 115 3528 (1982) (R = propargylic)

JOC 48 1159 (1983)

CatalystFeCl₃, H₂O

JCS 1887 (1963)

RuCl₂(PPh₃)₃

CL 115 (1978)

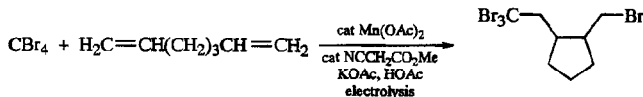
Coll Czech Chem Commun 61 774 (1996)

CuCl(amine)₂

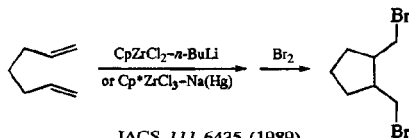
Coll Czech Chem Commun 61 774 (1996)

CuCl₂, H₂O

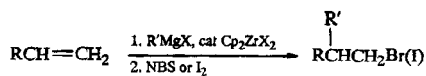
JCS 1887 (1963)



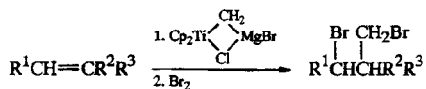
TL 33 213 (1992)



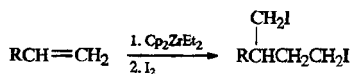
JACS 111 6435 (1989)



JACS 113 5079 (1991)

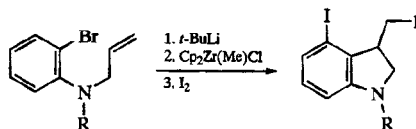


TL 24 3935 (1983)

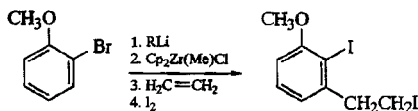


JOC 54 3521 (1989)

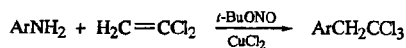
JACS 113 6266 (1991)



JACS 113 4685 (1991)

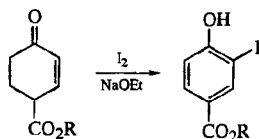


JACS 109 7137 (1987)



JOC 53 3637 (1988)

6. Miscellaneous Reactions



TL 36 8395 (1995)

4. HALOGENATION OF ALKYNES

See also page 410, Section 2, for additional preparations of vinylic halides.



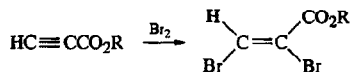
<u>X</u>	<u>Reagent(s)</u>	
Cl	NaOH, CCl ₄ (phase transfer)	Rocz 49 1779 (1975)
	HOCl	Ber 63 1868, 1886 (1930)
		Can J Chem 32 500 (1954)
		JACS 85 1648 (1963)
	PhSO ₂ Cl (on RC≡CNa)	Ann Chim [10] 16 309 (1931)
Br		JACS 56 1106 (1934)
		BSCF 1447 (1957)
	<i>n</i> -BuLi/Cl ₂	Tetr 22 965 (1966)
	<i>n</i> -BuLi/NCS	Syn 296 (1979)
		JACS 101 5101 (1979)
	CBr ₄ , PPh ₃	TL 31 3141 (1990)
	CCl ₃ Br, DBU	CL 73 (1978)
	Br ₂ , NaOH	JCS 2295 (1963)
	NaBr, NaOCl, (<i>n</i> -Bu ₄ N)HSO ₄	JOC 57 4555 (1992)
	HOBr	Ber 63 1868 (1930)
I		BSCF 1447 (1957)
		Arch Pharm 290 118 (1959)
		JACS 85 1648 (1963)
	Li, NH ₃ /CF ₃ Br	Tetr 23 4111 (1967)
	NBS, AgNO ₃	Angew Int 23 727 (1984)
	<i>n</i> -BuLi/NBS	JACS 94 4013 (1972)
	<i>n</i> -BuLi/Br ₂	Tetr 22 965 (1966)
		JACS 89 5086 (1967)
	BrCN (on RC≡CMgBr)	Ann Chim [10] 5 5 (1926)
	CuBr, (Me ₃ SiO) ₂	TL 32 2169 (1991)
	I ₂ , NH ₃	JACS 54 787 (1932); 55 2150 (1933); 56 1207 (1934)
		JCS 741 (1933)
	I ₂ , morpholine	JOC 27 3305 (1962)



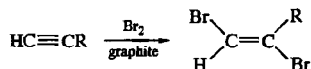
<u>X</u>	<u>Reagent(s)</u>	
I (continued)	I ₂ (on RC≡CCu)	Bull Acad Sci USSR, Div Chem Sci 2043 (1963)
	I ₂ , KI, KOH	JACS 77 176 (1955)
	I ₂ , Hg(OAc) ₂	Bull Acad Sci USSR, Div Chem Sci 869 (1968)
	I ₂ , cat CuI, K ₂ CO ₃ or Na ₂ CO ₃ , cat <i>n</i> -Bu ₄ NCl	CC 909 (1988)
	HOI	Ber 37 4412 (1904); 63 1886 (1930)
	NaOCH ₃ /I(py) ₂ BF ₄	Syn 661 (1987)
	[I(collidine) ₂]PF ₆	TL 36 2619 (1995)
	Li, NH ₃ / <i>n</i> -C ₃ F ₇ I	Tetr 23 4111 (1967)
	Na, NH ₃ /I ₂	JACS 55 2150 (1933); 56 1106 (1934)
	RLi/I ₂	Tetr 22 965 (1966)
		JACS 89 5086 (1967); 107 1028 (1985)
		JOC 51 5320 (1986); 57 6090 (1992)
	Na/I ₂	Ann 308 264 (1899)
	EtMgBr/I ₂	JACS 55 3453 (1933)
		JOC 49 515 (1984)
	NIS, AgNO ₃	Angew Int 23 727 (1984)
	ICN (on RC≡CMgBr)	Ann Chim [10] 5 5 (1926)
	CuI or ZnI ₂ , (Me ₃ SiO) ₂	TL 32 2169 (1991)
	<i>n</i> -BuLi/ZnI ₂ , (Me ₃ SiO) ₂	Syn 461 (1989)



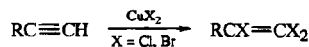
<u>X</u>	<u>Reagent(s)</u>	
F	F ₂	J Fluorine Chem 25 169 (1984)
Cl	Cl ₂ , SbCl ₅	JACS 62 1367 (1940)
	SO ₂ Cl ₂	BCSJ 54 2843 (1981)
	CuCl ₂ , LiCl	CC 925 (1975)
		JCS Perkin I 676 (1977)
Br	Br ₂	TL 1629 (1970); 34 4631 (1993)
		JOMC 372 183 (1989)
	Br ₂ , <i>i</i> -Pr ₂ NEt, molecular sieves	TL 34 4631 (1993)
	(<i>n</i> -Bu ₄ N)Br ₃	Can J Chem 64 603 (1986)
	(polymer-C ₆ H ₅ CH ₂ NMe ₃)Br ₃	Syn 143 (1980)
	CuBr ₂	JOC 30 587 (1965)
I	I ₂ , alumina	TL 29 35 (1988); 30 2069 (1989)
		JOC 53 4477 (1988)



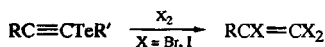
Org Syn 72 104 (1993)
TL 35 6913 (1994)



BCSJ 62 4053 (1989)







JOC 30 587 (1965)



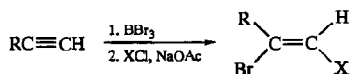
Syn Commun 20 2181 (1990)



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	Cl	NCS, HF	JOC 44 3872 (1979)
		NCS, HF-py	Syn 780 (1973)
	Br	N-chlorosaccharin, HF-py	SL 327 (1995)
		NBA, HF	JOC 35 1703 (1970)
		NBS, HF-py	Syn 780 (1973)
		 Br, HF-py	JOC 44 3872 (1979)
	I	 Br, HF-py	TL 32 69 (1991)
		NIS, HF-py	Syn 780 (1973)
	SePh	 NSePh, Et ₃ N·3HF	JOC 44 3872 (1979)
Cl	I	ICI	TL 31 2127 (1990)
			Tetr 30 579 (1994)
			JCS Perkin I 676 (1977)
			JOMC 372 183 (1989)
			JOC 56 3707 (1991)
			JCS Perkin I 676 (1977)
	I	CuCl ₂ , KI	CC 925 (1975)
		CuCl ₂ , I ₂	JCS Perkin I 676 (1977)
		 NSCl	TL 31 6213 (1990)
Br	I	IBr	TL 31 6213 (1990)
I	H, F, Cl, Br, I, OR, O ₂ CR, SR, SCN, pyridinium salt, Ar	I(py) ₂ BF ₄ ; Et ₃ SiH, F ⁻ , Br ⁻ , I ⁻ , ROH, RCO ₂ H, RSH, SCN ⁻ , py or ArH	Tetr 30 579 (1974)
			TL 27 3303 (1986); 31 2751 (RC≡CCl → RCX=CCl), 4207, 7375 (RC≡CSR → RCI=CXSR) (1990)
			JACS 110 5567 (1988)
			JOC 55 3104 (1990)



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
1 (cont'd)	Br, SCN SCN	I ₂ , CuO-HBF ₄ , LiBr or KSCN ISCN	CC 1491 (1987) BSCF 2569 (1964) Compt Rend 258 3878 (1964)

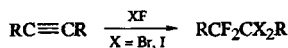


X = Br, I

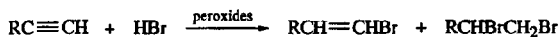
TL 26 1065 (1985)



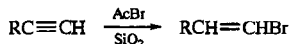
<u>X</u>	<u>Reagent</u>	
F	F ₂	JOC 32 4124 (1967) J Fluorine Chem 25 169 (1984)
	XeF ₂	JOC 39 2646 (1974)
	(NO)BF ₄ , py-HF	JOC 59 6493 (1994)
Cl	Cl ₂	Can J Chem 31 385 (1953)
	Cl ₂ , SbCl ₅	JACS 62 1367 (1940)
	SO ₂ Cl ₂	JACS 116 8116 (1994)



JOC 51 222 (1986)

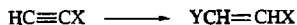


JACS 58 1806 (1936)



JOC 59 3102 (1994)

See also page 410, Section 2 for approaches involving hydrometallation/halogenation.



<u>X</u>	<u>Y</u>	<u>Reagents</u>	
COR	Cl, Br, I	LiY or NaI, HOAc	TL 27 4763 (1986) JOC 57 709 (1992)
	Br, I	LiBr or NaI, CF ₃ CO ₂ H	TL 27 4763 (1986)
CO ₂ H	Cl, Br, I	HY LiY, HOAc	JCS B 1466 (1970) JOC 57 709 (1992) TL 33 2535 (1992)
	I	HI, CuI	JACS 111 6729 (1989)

CO ₂ R	Cl, Br, I	LiY, HOAc	TL 31 7653 (1990); 33 2535 (1992)
	I	NaI, HOAc	JOC 57 709 (1992) TL 32 5329 (1991)
CONR ₂	Cl, Br, I	LiY, HOAc	JOC 57 709 (1992) TL 33 2535 (1992)
CN	Cl, Br, I	LiY, HOAc	JOC 57 709 (1992) TL 33 2535 (1992)

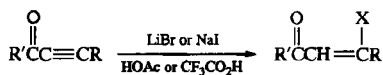


X	Reagent(s)	
Cl	HCl	Chimia 17 391 (1963) JACS 87 3151 (1965) Chem Ber 106 2001 (1973) TL 413 (1974) JOC 39 1124 (1974) JACS 62 1367 (1940) Helv 49 497 (1966) JOC 39 1124 (1974) JCS Perkin I 1797 (1977)
	HCl, SbCl ₅ HCl, cat HgCl ₂ HCl, Me ₄ NCl (Et ₄ N)HCl ₂	
Br	HBr	JACS 58 1806 (1936); 87 3151 (1965); 92 1416 (1970) Helv 54 2060 (1971) Ann 1137 (1979) Helv 49 497 (1966) Syn 805 (1980) JOC 59 1703 (1994) JOC 59 3102 (1994) JOC 39 3307 (1974) TL 24 731 (1983) JOC 58 5452 (1993)
	HBr, cat HgBr ₂ (Et ₄ N)HBr ₂ AcBr, Al ₂ O ₃ RLi/Me ₃ SiCl/HBr B-Br-9-BBN/HOAc	
I	HI	JACS 87 3151 (1965)
	HI, cat HgI ₂ I ₂ , Al ₂ O ₃ B-I-9-BBN/HOAc	Helv 49 497 (1966) TL 28 4497 (1987) TL 24 731 (1983) JACS 117 10391 (1995)
	PhNEt ₂ ·BI ₃ , HOAc NaI, Me ₃ SiCl, H ₂ O, CH ₃ CN	TL 31 1919 (1990) SL 675 (1990) TL 33 6839 (1992)

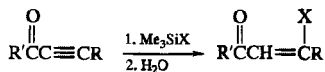


<u>X</u>	<u>Reagent(s)</u>	
F	HF	JCS 3490 (1952)
	(<i>n</i> -Bu ₄ N)H ₂ F ₃	BSCF 910 (1986)
	(polymer)H ₂ F ₃	BSCF 910 (1986)
Cl	HCl	JACS 88 5555 (1966); 89 2780 (1967); 90 2124 (1968)
		JOC 39 1124 (1974); 44 3316 (1979); 59 5048 (1994)
	HCl, AlCl ₃	JCS 3490 (1952)
	HCl, BiCl ₃	JACS 62 1367 (1940)
	HCl, ZnCl ₂	CC 857 (1972)
		JACS 98 3295 (1976)
	HCl, Me ₄ NCl	JACS 89 2780 (1967); 90 2124 (1968)
		JOC 39 1124 (1974)
	HCl, Al ₂ O ₃	JOC 59 3102 (1994)
	HCl, SiO ₂	JACS 112 7433 (1990)
		JOC 59 3102 (1994)
	(Et ₃ NH)HCl ₂	JCS Perkin I 1797 (1977)
	COCl ₂ , Al ₂ O ₃	JACS 112 7433 (1990)
	COCl ₂ , SiO ₂	JOC 59 3102 (1994)
	SOCl ₂ , Al ₂ O ₃	JOC 59 3102 (1994)
	SOCl ₂ , SiO ₂	JOC 59 3102 (1994)
Br	HBr	Ber 93 505 (1960)
		Helv 54 2060 (1971)
		Ann 1137 (1979)
	HBr, Fe	JOC 48 3894 (1983)
		TL 32 5861 (1991)
	HBr, AlBr ₃	JCS 3490 (1952)
	HBr, ZnBr ₂	Gazz Chim Ital 105 495 (1975)
	HBr, Al ₂ O ₃	JACS 112 7433 (1990)
		JOC 59 3102 (1994)
	HBr, SiO ₂	JOC 59 3102 (1994)
	AcBr, SiO ₂	JOC 59 3102 (1994)
	PBr ₃ , Al ₂ O ₃	JACS 112 7433 (1990)
I		JOC 59 3102 (1994)
		JOC 59 3102 (1994)
	HI	JCS 3490 (1952)
		JACS 112 7433 (1990)
		JOC 59 3102 (1994)
	NaI, Me ₃ SiCl, H ₂ O, CH ₃ CN	SL 675 (1990)
	NaI, <i>p</i> -TsOH	JOC 59 3102 (1994)
	AcI, Al ₂ O ₃	JACS 112 7433 (1990)
		JOC 59 3102 (1994)
	AcI, SiO ₂	JOC 59 3102 (1994)
	PI ₃ , Al ₂ O ₃	JOC 59 3102 (1994)
	PI ₃ , SiO ₂	JOC 59 3102 (1994)

See also page 410, Section 2 for analogous chemistry involving hydrometallation/halogenation.

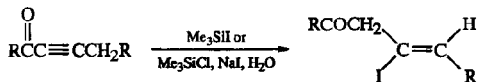


TL 27 4763 (1986)

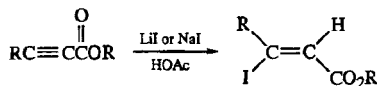


R = H or alkyl; X = Br, I

TL 27 4759, 4763 (1986)



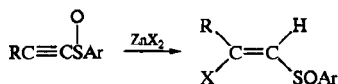
TL 35 2553 (1994)



TL 32 5329 (1991)

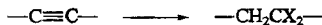
Can J Chem 72 1816 (1994)

SL 903 (1995)



X = Cl, Br, I

TL 33 6101 (1992)



X

F

Reagent

HF

Org Rxs 2 50 (1994) (review)

IACS 64 2289 (1942); 65 587

(1943)

 (HF)_x·py

JOC 44 3872 (1979)

 polyvinylpyridinium·(HF)_n

SL 267 (1990)

Cl

HCl

IACS 92 1416 (1970)

 HCl, SbCl₅

IACS 62 1367 (1940)

 SOCl₂, Al₂O₃

JOC 59 3102 (1994)

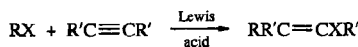
Br

HBr

JACS 57 2463 (1935)

 (COBr)₂, Al₂O₃

JOC 59 3102 (1994)



CC 857 (1972)

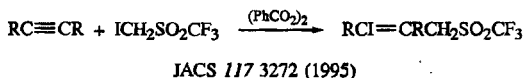
ICS Perkin I 2491 (1973); 353 (1974)

Gazz Chim Ital 105 495 (1975)

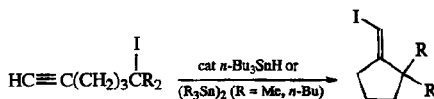
JCS Perkin II 1517 (1976)
 JACS 98 3295 (1976)
 JOC 44 3022 (1979)
 Angew Int 20 184 (1981)



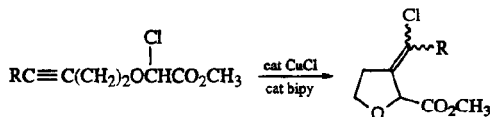
Et₃B TL 30 3155 (1989)
 (*n*-Bu₃Sn)₂, hν Tetr 47 6171 (1991)
 distannane polymer, hν SL 286 (1993)



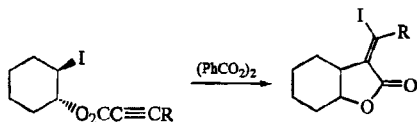
Δ JCS 588 (1951)
 TL 34 2931 (1993)
 hν JCS 3483 (1952); 1634 (1954)
 electrolysis J Fluorine Chem 16 553 (1980)
 CC 433 (1982)
 cat AIBN J Fluorine Chem 20 313 (1982)
 JOC 57 132 (1992)
 cat (*t*-BuO)₂ JOC 47 2251 (1982)
 cat Et₃B TL 30 3159 (1989)
 cat Ru₃(CO)₁₂, Fe₃(CO)₁₂, Fe₂(CO)₉ TL 25 303 (1984)
 or Co₂(CO)₈ plus cat amine
 cat Ni(CO)₂(PPh₃)₂ J Fluorine Chem 28 229 (1985)
 cat Pd(PPh₃)₄ CL 1895 (1986)
 Na₂S₂O₄ CC 631 (1994)
 TL 35 9141 (1994)



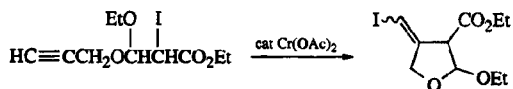
JACS 108 2489 (1986); 111 6265 (1989); 112 6738 (1990)
 TL 28 2477 (1987); 29 3691 (1988)



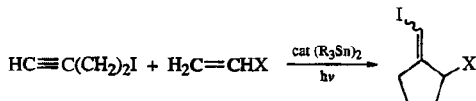
JOC 59 1993 (1994)



TL 29 1085 (1988)

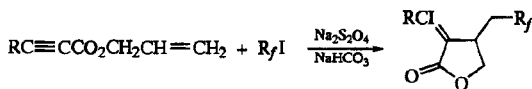


SL 861 (1991)

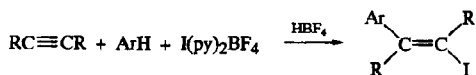


X = CHO, COR, CO₂R, CONR₂, SO₂R

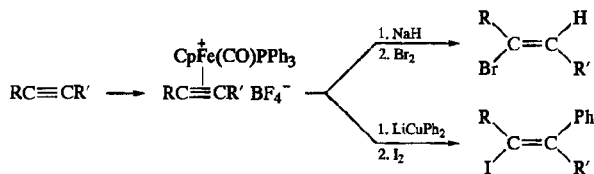
JACS 109 6538 (1987); 111 8872 (1989); 112 6738 (1990); 114 7007 (1992)



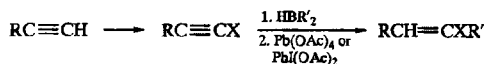
TL 35 613 (1994)



See page 657.

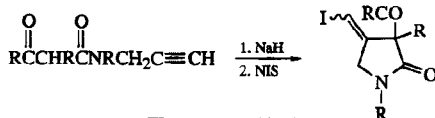


JACS 102 5923 (1980)

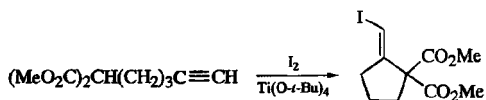


X = Cl, Br

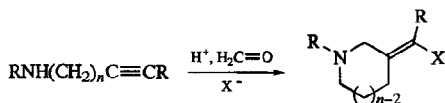
BCSJ 53 1652 (1980)



TL 31 1427 (1990)



JOC 58 3106 (1993)

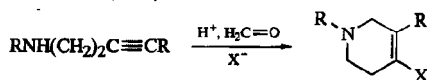
 $n=3-5$; $\text{X}=\text{Br}, \text{I}, \text{N}_3, \text{SCN}, \text{SPh}$

JACS 110 612, 5934 (1988); 114 368 (1992)

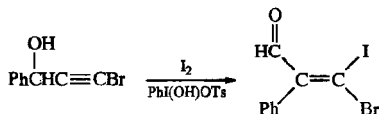
TL 29 901 (1988); 33 4103 (1992)

Org Syn 70 111 (1991)

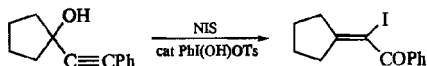
SL 995 (1992)

 $\text{X}=\text{Br}, \text{I}$

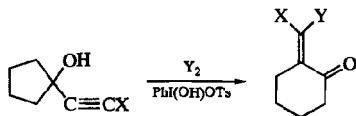
JACS 110 612 (1988)

ReagentsNBS, $\text{PhI}(\text{OH})\text{OTs}$ TL 33 2285 (1992) ($\text{R}=\text{I}$) I_2, HIO_3 TL 26 1967 (1985) ($\text{R}=\text{Ph}, \text{I}$)NIS, $\text{PhI}(\text{OH})\text{OTs}$ TL 33 2285 (1992) ($\text{R}=\text{Br}$)

TL 33 7705 (1992)



TL 34 8205 (1993)

 $\text{X}, \text{Y}=\text{Br}, \text{I}; \text{I}, \text{Br}$

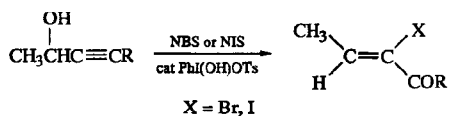
Tetr 49 1525 (1993)

TL 34 4277 (1993); 35 6431 (1994)

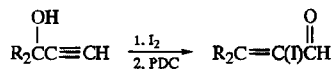
X

Br

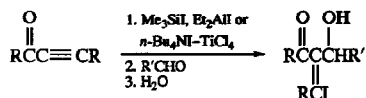
I



TL 32 2099 (1991)



TL 22 1041 (1981)

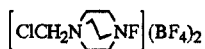


TL 27 4767 (1986)

X

Reagent(s)

F



JOC 60 259 (1995)

Br

NaBrO₃, NaHSO₃

JOC 59 5550 (1994)

5. INTERCONVERSION OF HALIDES

1. Aliphatic Halides



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	—	review	Org Rxs 2 49 (1944)
	Cl	HF	JACS 60 492 (1938)
		KF (phase transfer)	Syn 428 (1974)
			J Fluorine Chem 22 431 (1983)
			JOC 50 879 (1985)
		KF, HOCH ₂ CH ₂ OH	JACS 70 2596 (1948); 79 2311 (1957)
		KF, (HOCH ₂ CH ₂) ₂ O	Coll Czech Chem Commun 39 2616 (1974)
		KF, CH ₃ CN	CL 761 (1981)
		KF, CaF ₂ , CH ₃ CN	CC 791, 793 (1986)
		KF, CaF ₂ , sulfolane	CC 791 (1986)
		KF, <i>n</i> -Bu ₄ NBr, HCONH ₂	TL 27 1499 (1986)
		KF, ion exchange resin	JOC 54 4993 (1989)
		CsF, CaF ₂ , sulfolane	CC 791 (1986)
		<i>n</i> -Bu ₄ NF (no solvent)	JOC 49 3216 (1984)
		<i>n</i> -Bu ₄ NF, PPTS	TL 28 4419 (1987)
		(<i>n</i> -Bu ₄ N)HF ₂	TL 28 4733 (1987)
		(<i>n</i> -Bu ₄ N)Ph ₃ SiF ₂	JACS 117 5166 (1995)
		(resin-NMe ₃)F	Syn 472 (1976)
		(<i>n</i> -Bu ₃ MeP)F	TL 353 (1979)
		Mg/TsNFR	Tetr 36 1931 (1980)
		F ₂	JACS 106 452 (1984)
	Br	KF (phase transfer)	JOC 46 733 (1981)
			Syn 428 (1974)
			J Fluorine Chem 22 431 (1983)
		KF, cat 18-crown-6	JACS 96 2250 (1974)
			JOC 40 782 (1975); 57 2316 (1992)
		KF, HOCH ₂ CH ₂ OH	Org Syn Coll Vol 4 525 (1963)

$\text{RY} \longrightarrow \text{RX}$ (continued)

<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F (cont'd)	Br (cont'd)	KF, $(\text{HOCH}_2\text{CH}_2)_2\text{O}$	Coll Czech Chem Commun 39 2616 (1974)
		KF, $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$	CL 283 (1978)
		KF, HMPA	BSCF 334 (1969)
		KF, CH_3CN	CL 761 (1981)
		KF, CaF_2 , CH_3CN	CC 793 (1986)
		KF, CaF_2 , MeOH	JOC 59 3821 (1994)
		KF, <i>n</i> -Bu ₄ NF	Org Syn Coll Vol 8 258 (1993)
		KF, <i>n</i> -Bu ₄ NBr, HCONH ₂	TL 27 1499 (1986)
		KF, $(\text{Ph}_4\text{P})\text{Br}$	TL 28 111 (1987)
		$\text{R}_3\text{N} \cdot 3\text{HF}$ (R = Et, <i>n</i> -Bu)	J Fluorine Chem 15 423 (1980)
			TL 31 6527 (1990)
		<i>n</i> -Bu ₄ NF (no solvent)	JOC 49 3216 (1984)
		<i>n</i> -Bu ₄ NF, PPTS	TL 28 4419 (1987)
		$(n\text{-Bu}_4\text{N})\text{HF}_2$	TL 28 4733 (1987)
		$(n\text{-Bu}_4\text{NF})\text{Ph}_3\text{SiF}_2$	JACS 117 5166 (1995)
		(resin-NMe ₃)F	Syn 472 (1976)
			JCS Perkin I 2248 (1979)
		$(n\text{-Bu}_3\text{MeP})\text{F}$	TL 353 (1979)
			Tetr 36 1931 (1980)
		$(\text{Ph}_4\text{P})\text{HF}_2$	CC 672 (1985)
			J Fluorine Chem 30 251 (1985)
		Li/FCIO ₃	Ber 102 1944 (1969)
		Mg/TsNFR	JACS 106 452 (1984)
		AgF	JOC 40 782 (1975)
			TL 28 4003 (1987)
		AgF, HF-py	Syn 780 (1973)
		AgBF ₄	JACS 110 1303, 8591 (1988)
		HgF ₂	JACS 70 2310 (1948)
			JOC 40 782 (1975)
	I	(resin-NMe ₃)F	JCS Perkin I 2248 (1979)
		$(n\text{-Bu}_4\text{N})\text{HF}_2$	TL 28 4733 (1987)
		$(n\text{-Bu}_4\text{NF})\text{Ph}_3\text{SiF}_2$	JACS 117 5166 (1995)
		$(\text{Ph}_4\text{P})\text{HF}_2$	J Fluorine Chem 30 251 (1985)
		AgF	JOC 40 782 (1975)
		AgF, HF-py	Syn 780 (1973)
		HgF ₂	JOC 40 782 (1975)
		XeF ₂	JOC 57 2850 (1992); 58 7876 (1993)
			JACS 114 10730 (1992); 115 10174 (1993)
			TL 31 4973 (1990)
Cl	F Br	HCl, H ₂ O	JCS 3173 (1955)
		LiCl, CH_3COCH_3	CC 1250 (1986)
		NaCl, H ₂ O, phase transfer	BSCJ 49 1989 (1976)
		cat NaCl, <i>i</i> -PrCl	Syn 472 (1976)
		(resin-NMe ₃)Cl	TL 763 (1974)
		graphite-SbCl ₅	

		FeCl ₃	JACS 110 1303, 8591 (1988)
		AgO ₂ CCF ₂ Cl	TL 3447 (1970)
I		cat NaCl, <i>n</i> -PrCl	BCSJ 49 1989 (1976)
		Cl ₂	TL 27 6055 (1986)
		PhICl ₂	TL 27 6055 (1986)
		graphite-SbCl ₅	TL 763 (1974)
Br	—	review	Houben-Weyl, Vol V/4, p 354
	F	HBr, H ₂ O	TL 31 4973 (1990)
	Cl	HBr, H ₂ O	TL 31 4973 (1990)
		HBr, cat FeBr ₃	CC 1013 (1987)
			JOC 54 3028 (1989)
		LiBr, CH ₃ COCH ₃	JACS 77 4903 (1955)
		LiBr, phase transfer	CC 1250 (1986)
		NaBr, CH ₃ OH	JACS 39 1730 (1917); 77 165 (1955)
		NaBr, ion exchange resin	JOC 54 4993 (1989)
		cat NaBr, EtBr	BCSJ 49 1989 (1976)
		CaBr ₂	BSCF 1 860 (1934)
		CaBr ₂ , (R ₄ N)Br	Syn 34 (1984)
		AlBr ₃	JACS 78 491 (1956)
		FeBr ₃	JOC 54 3028 (1989)
		(resin-NMe ₃)Br	Syn 472 (1976)
I		cat NaBr, EtBr	BCSJ 49 1989 (1976)
		<i>t</i> -BuLi/Br ₂	JACS 114 10730 (1992)
		<i>t</i> -BuLi/BrCH ₂ CH ₂ Br	JOC 55 5404 (1990)
		Mg/Br ₂	JACS 41 287 (1919)
		Br ₂	TL 27 6055 (1986)
I	—	review	Houben-Weyl, Vol V/4, p 595
	F	HI, H ₂ O	TL 31 4973 (1990)
		Me ₃ SiI	JOC 46 3727 (1981)
	Cl	HI, H ₂ O	TL 31 4973 (1990)
		HI, cat FeI ₃	CC 1013 (1987)
		NaI, CH ₃ COCH ₃	JACS 109 5491 (1987)
		NaI, FeCl ₃	JCS Perkin I 416 (1976)
		NaI, FeCl ₃ or HgCl ₂	TL 2691 (1974)
		NaI, ZnCl ₂	JCS Perkin I 416 (1976)
		cat NaI, MeI	BCSJ 49 1989 (1976)
		KI, (<i>n</i> -Bu ₄ P)I, silica	Syn 952 (1979)
		Me ₃ SiI	JOC 46 3727 (1981)
		I ₂ , cat Fe(CO) ₅	JOC 54 3028 (1989)
Br		HI, H ₂ O	TL 31 4973 (1990)
		NaI, phase transfer catalyst	JOC 50 5828 (1985)
		NaI, CH ₃ COCH ₃	JCS 1605 (1936)
		NaI, HMPA	JACS 90 6225 (1968)
		NaI, benzo-15-crown-5	CC 879 (1974)
		NaI, ion exchange resin	JOC 54 4993 (1989)
		NaI, (Me ₄ N)Cl-silica	JOC 55 2952 (1990)
		cat NaI, MeI	BCSJ 49 1989 (1976)
		KI, DMF	JOC 34 3519 (1969)



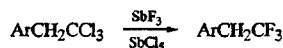
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
I (cont'd)	Br (cont'd)	KI, crown ether	CC 879 (1974)
		KI, (n-Bu ₄ P)I, silica	Syn 952 (1979)
		(resin-NMe ₃)I	Syn 472 (1976)
		Mg/I ₂	JACS 41 287 (1919)
		Mg/HgBr ₂ /I ₂	JACS 61 1585 (1939); 91 5774 (1969)
		Et ₂ Zn, cat FeCl ₃ or MnX ₂ (X = Cl, Br), cat CuCl/I ₂	TL 35 1177 (1994)



JOC 53 1331 (1988)



<u>X</u>	<u>Reagent(s)</u>	
Cl	Hg, HF-py	JOC 44 3872 (1979)
Cl, I	AgBF ₄	TL 28 5347 (1987)



JOC 53 3637 (1988)

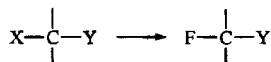


<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	Cl	AlCl ₃ , CS ₂	TL 30 3825 (1989)
			JOC 56 103 (1990); 60 2721 (1995)
Cl	F	AgBF ₄ FCCl ₃ , AlCl ₃	TL 28 5347 (1987)
			TL 30 3825 (1989)
			JOC 56 103 (1990)



<u>X</u>	<u>Reagents</u>
Cl	HOSO ₂ Cl, TaF ₅ or NbF ₅
Br	HBr, HF, BF ₃

JOC 60 3423 (1995)



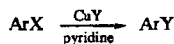
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
Cl	COR	HgO, HF-py	JOC 44 3872 (1979)
Br	OR	ZnF ₂ , bipy	SL 162 (1994)
	COR	Et ₃ N·3HF, Et ₃ N	TL 31 6527 (1990)
		polymer-H _n F _{n+1} (n = 0, 1, 2)	JOC 54 5380 (1989)
		HgO, HF-py	JOC 44 3872 (1979)
	CO ₂ H	HgO, HF-py	JOC 44 3872 (1979)

2. Vinylic Halides



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	I	<i>t</i> -BuLi / PhSO ₂ NF- <i>t</i> -Bu	IACS 108 2445 (1986)
Cl, Br	I	CuX	JOMC 93 415 (1975)
I	Br	KI, Zn, NiBr ₂	CL 1435 (1978)
		KI, NiBr ₂ , electrolysis	TL 27 3497 (1986)

3. Aromatic Halides

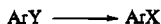


X = Br, I; Y = Cl, Br, I

Proc Chem Soc 113 (1962)

JCS 1097, 1108 (1964)

Tetr 40 1433 (1984) (review)

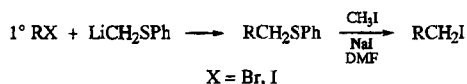


<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	Cl	KF, DMF or DMSO	JACS 78 6034 (1956)
			JOC 28 1666 (1963)
		KF, sulfolane	JCS 6264 (1965)
			J Fluorine Chem 46 529 (1990)
			JOC 56 6406 (1991)
		KF, (Ph ₄ P)Br	TL 28 111 (1987)
			J Fluorine Chem 44 291 (1989)
		KF, (Ph ₄ P)Br, 18-crown-6 or poly(ethylene glycol)	CL 1355 (1988)
		KF, cat (Ph ₄ P)Br,	CL 2213 (1989)
		<i>o</i> -C ₆ H ₄ (COCl) ₂	
		KF (freeze dried)	TL 30 1271 (1989)



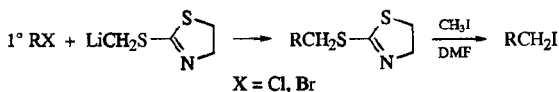
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F (<i>cont'd</i>)	Cl (<i>cont'd</i>)	KF, cat aminopyridinium polymer	TL 30 7199 (1989)
		(<i>n</i> -Bu ₄ N)HF ₂	TL 28 4733 (1987)
	Br	(<i>n</i> -Bu ₄ P)F·(HF) _n (<i>n</i> = 1, 2)	SL 345 (1992)
		(Ph ₄ P)HF ₂	J Fluorine Chem 30 251 (1985)
		KF, sulfolane	JCS 6264 (1965)
		(<i>n</i> -Bu ₄ P)F·HF	SL 345 (1992)
Cl	Br	Li/PClO ₃	Ber 102 1944 (1969)
		Mg/TsNF- <i>t</i> -Bu	JACS 106 452 (1984)
		NaOCl, cat Ni tetraphenylporphyrin, cat (<i>n</i> -Bu ₃ NCH ₂ Ph)Br	JOC 56 1344 (1991)
	I	CuCl	BSCF 720 (1973)
		Mg/Ph ₃ PCl ₂	JOC 32 3710 (1967)
Br	I	CCl ₄ , hν	JOC 35 528 (1970)
		Mg/Br ₂	JACS 41 287 (1919)
I	Cl	NaI, DMF	JOC 23 305 (1958)
		NaI, AcCl	TL 31 6757 (1990) (pyridines)
	Br	CuI-alumina or charcoal	CC 1409 (1987)
		NaI, CH ₃ COCH ₃	JOC 28 218 (1963)
		NaI, AcCl	TL 31 6757 (1990) (pyridines)
		NaI, cat CuSO ₄	JOC 60 8324 (1995)
		KI, I ₂ , Ni, DMF	JOC 52 691 (1987)
		KI, NiBr ₂ , Zn	CL 191 (1978)
		KI, NiBr ₂ , <i>n</i> -Bu ₃ P	BCSJ 53 3691 (1980)
		KI, NiBr ₂ , electrolysis	TL 27 3497 (1986)
		KI, CuI, HMPA	JACS 108 3150 (1986)
		KI, CuI, DMF	JOC 57 2093 (1992)
		KI, cat Pd(OAc) ₂ , NaOEt, HMPA	BCSJ 48 3298 (1975)
		CuI-alumina or charcoal	CC 1409 (1987)
		Mg/I ₂	JACS 41 287 (1919)
		Mg/ICN	JOC 3 55 (1938)
			Ann Chim 4 28 (1915)

4. Homologation of Halides

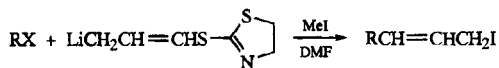


X = Br, I

TL 5787 (1968)

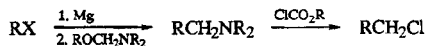


TL 2743 (1972)

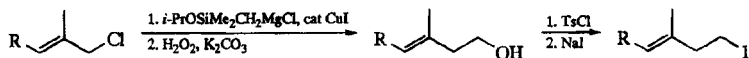


TL 2743 (1972)

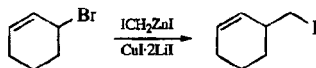
Org Syn Coll Vol 6 704 (1988)



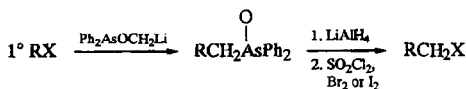
TL 28 427 (1987)



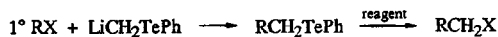
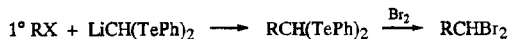
JOC 52 4885 (1987)



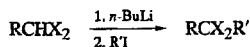
JOC 54 5202 (1989)

 $\text{X} = \text{Cl}, \text{Br}, \text{I}$

Ber 115 645 (1982)

 $\text{X} = \text{Cl}, \text{Br}, \text{I}; \text{reagent} = \text{SOCl}_2, \text{Br}_2, \text{I}_2, \text{MeI-NaI}$ 

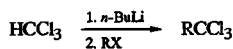
CL 1081 (1982)

 $\text{X} = \text{Cl}, \text{Br}$

BSCF 765 (1977)

Syn 502 (1979)

Compt Rend II 294 37 (1982)



JOC 55 1281 (1990)



TL 29 1699 (1988)

JOC 53 4720 (1988)



JOC 53 4720 (1988)



R = aryl, X = Br; R = alkyl, X = I

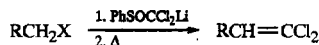
Y

F

TL 24 725 (1983)

Cl

TL 617 (1979)



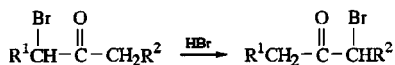
TL 24 527 (1983)

5. Rearrangement of Halides

See also page 647, Section 5.

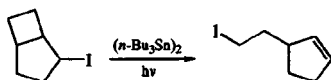


JCS 2720 (1959)

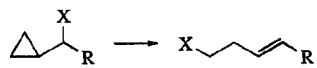


JOC 19 538 (1954)

JCS 1342 (1955)



TL 28 5063 (1987)



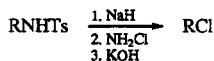
See page 291, Section 41.

6. HALOGENATION OF NITROGEN COMPOUNDS

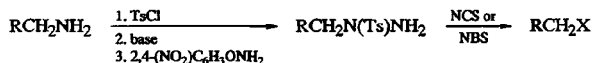
See page 736, Section 7 for the halogenation of amides.



<u>X</u>	<u>Reagents</u>	
F	HF-py, NaNO ₂	IOC 44 3872 (1979) Helv 64 2528 (1981) TL 32 4267 (1991)
Cl	HCl, NaNO ₂	JACS 76 6054 (1954) IOC 51 242 (1986); 57 3380 (1992) Org Syn Coll Vol 8 119 (1993) TL 36 2995 (1995)
	KCl, NaNO ₂ , CF ₃ CO ₂ H	JACS 112 6388 (1990)
	KCl, NOBF ₄	JACS 112 6388 (1990)
Br	HBr, NaNO ₂	TL 28 1993 (1987) IOC 58 1159 (1993)
	LiBr, NaNO ₂ , CF ₃ CO ₂ H	JACS 112 6388 (1990)
	LiBr, NOBF ₄	JACS 112 6388 (1990)
	NaBr, NaNO ₂ , H ₂ SO ₄	IOC 57 4352 (1992)
	KBr, NaNO ₂ , H ₂ SO ₄	BSCJ 26 53 (1953); 52 949 (1979) TL 36 8303 (1995)

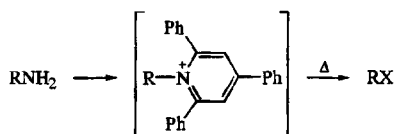


IOC 57 3772 (1992)



X = Cl, Br

TL 35 7911 (1994)

XR

F

1° alkyl, benzylic

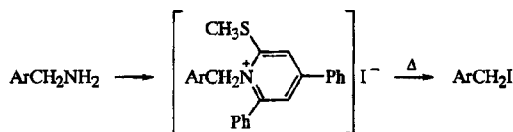
JCS Perkin I 2901 (1980)

Br

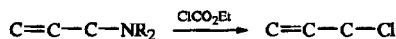
1° alkyl, benzylic

JCS Perkin I 1890 (1980)

I

1°, 2° alkyl; benzylic; aryl;
heterocyclicSyn 634 (1977)
JCS Perkin I 433 (1979)

Syn 853 (1980)



Syn 786 (1977)

SL 505 (1990)



Reviews:

Chem Rev 40 251 (1947)

Quart Rev 6 358 (1952)

"The Chemistry of Diazonium and Diazo Groups," Ed. S. Patai, J. Wiley, New York (1978), Part 1,
pp 288-290XReagents

F

 $\text{HNO}_2/\text{BF}_4^-/\Delta$

Ber 60 1186 (1927)

Org Rxs 5 193 (1949)

JOC 53 3513 (1988)

JOC 44 3872 (1979)

Org Syn Coll Vol 5 133 (1973)

TL 31 3019 (1990)

 $[\text{C}_5\text{H}_5\text{NH}]\text{F}(\text{HF})_x/\text{NaNO}_2$ HCl, NaNO_2 /HPF₆, Δ NaBF_4 , *t*-BuSNO or *t*-BuSNO₂

Cl

HCl, NaNO_2 /Cu

Ber 23 1220 (1890)

HCl, NaNO_2 /CuClOrg Syn Coll Vol 1 170 (1941); 2
130 (1943)HCl, NaNO_2 /CuCl, CuCl₂

JOC 59 5535 (1994)

 H_2SO_4 , NaNO_2 /CuCl

Org Syn Coll Vol 4 160 (1963)

JACS 108 1000 (1986)

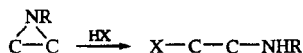
 NaNO_2 , Me₃SiCl, cat

TL 33 3167 (1992)

(PhCH₂NEt₃)Cl*t*-BuONO, CuCl₂

JOC 42 2426 (1977)

	AmONO, CCl ₄	JOC 45 3969 (1980) Syn 670 (1982)
	<i>t</i> -BuSNO, CuCl ₂	BCSJ 53 1065 (1980)
	<i>t</i> -BuSNO ₂ , CCl ₄	BCSJ 53 2023 (1980)
	HgCl ₂ , Δ	Ber 65 1605 (1932)
Br	HBr, NaNO ₂ /Cu	Org Syn Coll Vol 1 135 (1941)
	HBr, NaNO ₂ /CuBr	Org Syn Coll Vol 3 185 (1955) JACS 109 3378 (1987)
	KBr, H ₂ SO ₄ /NaNO ₂ /Cu	Ber 23 1220 (1890)
	H ₂ SO ₄ , NaNO ₂ /CuBr	JOC 51 1339 (1987)
	HNO ₂ /Et ₂ NH, Me ₃ SiCl, LiBr	JOC 46 5239 (1981)
	NaNO ₂ , Me ₃ SiBr, cat (PhCH ₂ NEt ₃)Cl	TL 33 3167 (1992)
	<i>t</i> -BuONO, CuBr ₂	JOC 42 2426 (1977); 57 6380 (1992)
	AmONO, HCBBr ₃	JCS C 1249 (1966) JOC 45 3969 (1980) Syn 670 (1982)
	<i>t</i> -BuSNO, CuBr ₂	BCSJ 53 1065 (1980)
	<i>t</i> -BuSNO ₂ , HCBBr ₃	BCSJ 53 2023 (1980)
	HgBr ₂ , Δ	Ber 65 1605 (1932)
I	HNO ₂ /pyrrolidine/KI, H ⁺	Syn 572 (1980)
	HNO ₂ /Et ₂ NH/Me ₃ SiCl, NaI	JOC 46 5239 (1981)
	NaNO ₂ , Me ₃ SiI, cat (PhCH ₂ NEt ₃)Cl	TL 33 3167 (1992)
	HCl, NaNO ₂ /KI	JOC 51 1339 (1987) JACS 114 6227 (1992)
	H ₂ SO ₄ , NaNO ₂ /KI, Cu	Org Syn Coll Vol 2 355 (1943)
	KI, H ₂ SO ₄ /NaNO ₂ /Cu	Ber 23 1220 (1890)
	AmONO, I ₂	JOC 33 1636 (1968)
	AmONO, CH ₂ I ₂	JOC 45 3969 (1980) Syn 670 (1982)
	<i>i</i> -AmONO, CH ₂ I ₂	JCS Perkin I 859 (1987) JOC 55 2543 (1990)
	<i>t</i> -BuSNO ₂ , I ₂	BCSJ 53 2023 (1980)
	I ₂ , DMSO on (ArN ₂)BF ₄	Syn Commun 11 639 (1981)



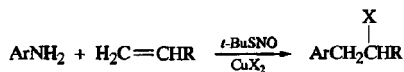
See page 802, Section 4.



X = Cl, Br; R' = *t*-Bu, *i*-Am

CC 433 (1976)

JACS 117 8017 (1995)



X = Cl, Br

BCSJ 53 1065 (1980)

XReagent(s)

F

KF, DMF

JACS 78 6034 (1956)

KF, cat (Ph₄P)Br,

CL 2213 (1989)

o-C₆H₄(COCl)₂(n-Bu₄P)F·HF

SL 345 (1992)

(Ph₄P)HF₂

J Fluorine Chem 30 251 (1985)

Cl

hv, HCCl₃, HCl

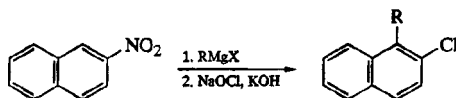
TL 4603 (1969)

SOCl₂

Monatsh 36 723 (1915)

PhPCl₄, PhPOCl₂

JOC 53 2858 (1988)



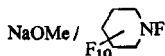
Syn 616 (1980)

XReagents

F

NaOMe / AcOF

JOC 59 6800 (1994)



J Fluorine Chem 52 389 (1991)

(n-Bu₄N)OH / TsNF-t-Bu

JACS 106 452 (1984)

Cl

NaOH / Cl₂

JOC 5 100 (1940); 27 2930 (1962)

KOH / Cl₂

JOC 16 1503 (1951); 42 3764 (1977)

KOH / NCS

Syn 828 (1986)

Br

NaHCO₃ / Br₂

CC 1240 (1980)

NaOMe / Br₂

JACS 71 2671 (1949); 73 3831 (1951)

NaOH / Br₂

JOC 5 100 (1940)

KOH / Br₂

JCS 2976 (1960)

KOH / NBS

JOC 16 1503 (1951); 42 3764 (1977)

Syn 828 (1986)

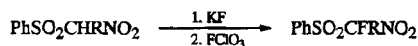
I

NaOH / I₂, KI

JOC 5 100 (1940)

KOH / I₂

JOC 16 1503 (1951); 42 3764 (1977)



JOC 54 5453 (1989)



X

Reagent(s)

F

HF

Bull Acad Sci USSR, Div Chem Sci 363 (1956)

Ber 89 864 (1956)

JACS 79 1959 (1957)

Chem Ind 394 (1957)

J Fluorine Chem 23 482 (1983)

Syn 896 (1974)

JOC 44 3872 (1979)

 $[\text{C}_5\text{H}_5\text{NH}]\text{F}(\text{HF})_x$

Cl

HCl

Helv 27 1108 (1904)

JCS 1310 (1928)

JACS 68 2220 (1946); 72 3477 (1950); 74

2082 (1952); 76 1185 (1954)

Org Syn Coll Vol 3 119 (1955)

TL 2367 (1977); 29 2231 (1988)

Br

HBr

JOC 12 767, 776 (1947); 18 868 (1953); 53

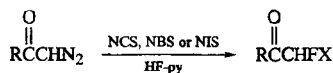
3803 (1988)

JCS 278 (1948)

JACS 74 2082, 2550 (1952); 117

10220 (1995)

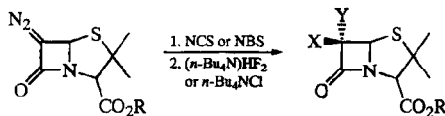
TL 36 5453 (1995)



X = Cl, Br, I

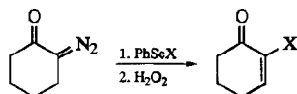
Syn 896 (1974)

JOC 44 3872 (1979)



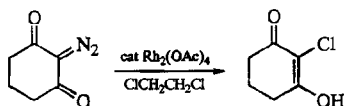
X, Y = Cl, F; Cl, Cl; Br, F

JOC 55 3674 (1990)

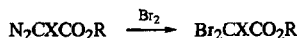


X = Cl, Br

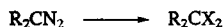
JOC 59 2748 (1994)



JOC 60 2112 (1995)

X = H, COR, CO₂R

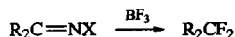
Bull Korean Chem Soc 13 226 (1992)



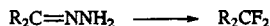
<u>X</u>	<u>Reagent(s)</u>	
F	F ₂	JCS Perkin I 1224 (1978) JOC 46 3917 (1981) J Fluorine Chem 25 157 (1984) J Fluorine Chem 23 482 (1983) JCS Perkin I 1224 (1978)
	F ₂ , KF CF ₃ OF	
Cl	Cl ₂	J Prakt Chem [2] 38 433 (1888) Ber 86 1467 (1953); 87 971 (1954)
Br	Br ₂	J Prakt Chem [2] 38 433 (1888) Ber 66 1541 (1933); 86 1467 (1953); 87 971 (1954) JACS 72 3655 (1950) Bull Korean Chem Soc 13 226 (1992)
I	I ₂	Ber 18 1283 (1885); 19 2460 (1886); 27 1888 (1894); 28 2374 (1895); 35 897 (1902); 60 1364 (1927); 66 1541 (1933) J Prakt Chem [2] 38 422, 433 (1888) Ann 325 143 (1902); 394 36 (1912) JACS 65 1458, 1516 (1943)



<u>X</u>	<u>Reagents</u>	
F	NOBF ₄ , py·(HF) _n	SL 425 (1994)
Cl	Cl ₂ , AlCl ₃	JOC 58 1939 (1993)

X = OCH₃, 2,4-(NO₂)₂C₆H₃NH

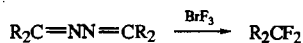
JOC 59 2918 (1994)



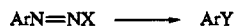
F₂ J Fluorine Chem 25 157 (1984)

IF JACS 109 896 (1987)
JOC 56 4695 (1991)

NBS, py·(HF)_n or polyvinylpyridinium(HF)_n SL 594 (1990)

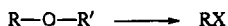


JOC 59 2918 (1994)



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
NR ₂	F	HF, py	CC 914 (1979)
	Br	LiBr, Me ₃ SiCl	JOC 46 5239 (1981)
	I	I ₂	TL 35 5539 (1994)
		CH ₃ I, Δ	TL 32 2465 (1991)
		NaI, Me ₃ SiCl	JOC 46 5239 (1981)
		NaI, sulfonic acid resin	JOC 48 4394 (1983)
SPh	F	HF, py, AgF or AgNO ₃	JOC 56 4993 (1991)

7. HALOGENATION OF ETHERS



<u>X</u>	<u>Reagent(s)</u>	
Cl	BCl ₃	Chem Ind 609 (1963) (R' = Me)
	PhCOCl, cat <i>n</i> -Bu ₃ SnCl, cat PhCH ₂ PdCl(PPh ₃) ₂	JOC 47 1215 (1982) (R = PhCH ₂)
	R''COCl, Zn	JOC 60 745 (1995)
Br	HBr, H ₂ SO ₄	JOC 52 5480 (1987); 58 898 (1993)
	HBr, HOAc	Syn 771 (1978)
	HBr, cat [<i>n</i> -C ₁₆ H ₃₃ P(<i>n</i> -Bu) ₃]Br	Syn 771 (1978)
	BBr ₃	Chem Ind 609 (1963) (R' = Me)
	<i>B</i> -Br-9-BBN	JOC 53 3912 (1988)
	BF ₃ ·OEt ₂ / AcBr	JOMC 156 221 (1978)
	Ph ₃ PBr ₂	(R = 3° > 2° > 1° alkyl)
		JACS 111 6311 (1989) (R = benzylic)
		Chem Ind 200 (1969) (R' = <i>t</i> -Bu)
		JOC 58 5900 (1993)
I	BI ₃ ·PhNEt ₂	TL 31 6977 (1990)
	Me ₃ SiI	JOC 42 3761 (1977)
	H ₂ SiI ₂	JOC 52 4846 (1987)

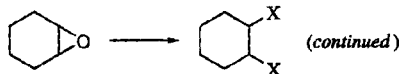
See also page 1013, Section 7, for cleavage of ethers to alcohols plus organic halides.



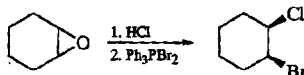
HCl, ZnCl ₂	JACS 107 6546 (1985)
CH ₃ COCl, cat SnCl ₄	JACS 107 6546 (1985)



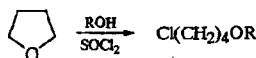
<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry</u>	
Cl	Ph ₃ PCl ₂	cis	JOC 41 3279 (1976)
			Org Syn Coll Vol 6 424 (1988)



<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry</u>	
Cl (continued)	SOCl ₂ , py	cis	Can J Chem 44 2339 (1966)
Br	Ph ₃ PBr ₂	cis + trans	JOC 41 3279 (1976)



JOC 41 3279 (1976)



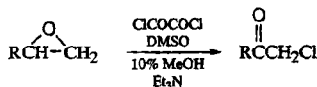
SL 233 (1991)



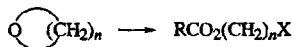
See page 1027, Section 3.



TL 36 7287 (1995)

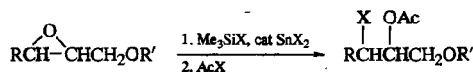


TL 33 6021 (1992)



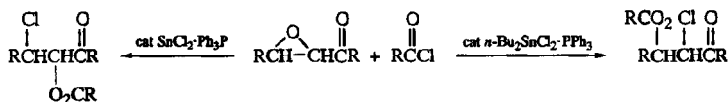
<u>X</u>	<u>n</u>	<u>Reagent(s)</u>	
Cl	2	RCOCl, [(n-Bu ₃ N) ₃ C]Cl-silica	JOC 59 4925 (1994)
		PhCOCl, cat n-Bu ₃ SnCl, cat PhCH ₂ PdCl(PPh ₃) ₂	JOC 47 1215 (1982)
		PhCOCl, cat n-Bu ₂ SnCl ₂ , cat Ph ₃ P	TL 27 3021 (1986)
		RCOCl, cat CoCl ₂	TL 29 4985 (1988)
	2, 4	RCOCl, Zn	JOC 60 745 (1995)
	3-5	RCOCl, cat K[Pt(C ₂ H ₄)Cl ₃]	JOC 48 751 (1983)
	4	RCOCl	TL 35 1553 (1994)
		RCOCl, cat Mo(CO) ₆	JOC 38 64 (1973)
		CH ₃ COCl, cat Rh ₂ (C ₂ H ₄) ₄ Cl ₂	JOC 48 751 (1983)
		RCOCl, cat ZnCl ₂	IACS 61 2667 (1939)
			TL 35 1553 (1994)

Br	2, 4, 5	(CH ₃ CO) ₂ O, MgBr ₂	JOC 40 3571 (1975)
	4	CH ₃ COBr	TL 3813 (1965)
		CH ₃ COBr, cat K[Pt(C ₂ H ₄)Cl ₃]	JOC 48 751 (1983)
		CH ₃ COBr, cat ZnCl ₂	JCS 1536 (1954) JOC 51 3372 (1986)
I	4, 5	RCOCl, NaI	TL 23 681 (1982)
			TL 35 1553 (1994)



R' = alkyl, aryl, SiR₃, COR; X = Cl, Br

SL 1004 (1995)



TL 33 7149 (1992)



<u>X</u>	<u>Reagent(s)</u>	<u>R</u>	
F	PhPF ₄	1°, 2°, 3° alkyl	TL 847 (1972) Tetr 29 1877 (1973) BSCF 2861 (1974) JOC 44 3406 (1979)
	<i>n</i> -Bu ₄ NF or (PhCH ₂ NMe ₃)F, RSO ₂ F (R = Me, <i>p</i> -Tol), molecular sieves	1° alkyl, 1° benzylic	TL 26 4207 (1985)
	Ph ₃ P·Br ₂	1°, 2° alkyl	JOC 51 4941 (1986)
	CBr ₄ , PPh ₃ , CH ₃ COCH ₃	1° alkyl, allylic, benzylic; 2° alkyl	TL 28 1697 (1987)
I	Me ₃ SiCl, NaI	1°, 2°, 3° alkyl; 1° benzylic	Syn 379 (1979)
	Me ₃ SiI	1° alkyl	SL 279 (1992)
	Ph ₃ PClI	R ₇ CH ₂	TL 35 1941 (1994)



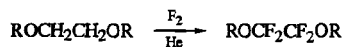
Y = R, OR

<u>X</u>	<u>Reagent(s)</u>
Cl	Me ₃ SiCl, cat BiCl ₃
Br	Me ₃ SiBr
I	Me ₃ SiCl, NaI

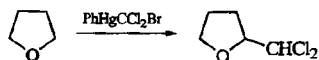
JOC 59 2238 (1994)



See page 727, Section 2.



JACS 116 5172 (1994)



JACS 87 4259 (1965)

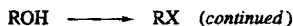
JOC 35 1993 (1970)

8. HALOGENATION OF ALCOHOLS


Review: *Tetr* 36 1901 (1980) (allylic alcohols)

1. Direct Methods

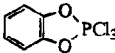
<u>X</u>	<u>Reagent(s)</u>	ROH \longrightarrow RX
F	HF, KF py·(HF) _n	JACS 85 1609 (1963) (3° benzylic) Syn 786 (1973) (2°, 3° alkyl) IOC 44 3872 (1979) (2°, 3° alkyl) Org Syn Coll Vol 6 628 (1988) (3° alkyl)
	polyvinylpyridinium·(HF) _n SF ₄ , HF	SL 267 (1990) (1°, 2° alkyl) IOC 40 3808 (1975) (1°, 2° alkyl); 55 5291 (1990) (1° alkyl)
	Et ₂ NSF ₃	IOC 40 574 (1975) (1°, 2°, 3° alkyl; 1°, 2° allylic; 1° benzylic; 2° propargylic); 43 1090 (1978); 44 3406 (1979); 52 4804 (1987); 53 1040 (1988) (all 2° alkyl); 54 1459 (1989) (2° allylic); 55 243 (1990) (2° allytic); 56 3229 (2° alkyl), 3449 (2° propargylic) (1991); 57 553 (1992) (2° alkyl); 59 1166, 8034 (1994) (both 2° alkyl)
		TL 573 (1977) (1° alkyl); 1823 (1979) (2° alkyl); 28 3891 (1987) (2° alkyl); 29 5217 (1988) (2° alkyl); 30 5791 (1989) (1° alkyl); 31 7403 (1990) (2° alkyl); 32 5963 (1991) (3° allylic, rearrangement); 33 1509 (1992) (2° alkyl); 35 41, 7569, 7573 (all 2° alkyl), 8587 (1° allytic) (1994); 36 1609 (2° alkyl), 4223 (2°, 3° allytic), 7449 (2° alkyl) (1995)
		CC 65 (1979) (2° alkyl)
		J Fluorine Chem 23 557 (1983) (2° alkyl)
		J Carbohydr Chem 4 587 (1985) (2° alkyl)
		JACS 109 3046 (1987) (2° allytic); 110 8686 (1988) (2° benzylic); 112 4258 (1990) (2° alkyl)

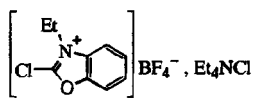
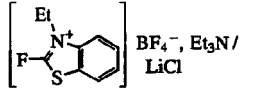


X	Reagent(s)	
F (continued)		Org Rxs 35 513 (1988) (review)
		Org Syn Coll Vol 6 835 (1988) (1° benzylic)
	(Me ₂ N) ₂ SF ₂	JOC 40 574 (1975) (2° alkyl, 1° allylic)
	<i>n</i> -Bu ₄ NF, RSO ₂ F (R = Me, <i>p</i> -Tol), molecular sieves	TL 26 4207 (1985) (1° alkyl)
	SeF ₄ , py	JACS 96 925 (1974) (1°, 2°, 3° alkyl)
	PhPF ₄	Chem Pharm Bull 21 867 (1973) (1°, 2° alkyl); 23 196 (1975) (2° alkyl)
		BSCF 2861 (1974) (2° alkyl)
	Ph ₂ PF ₃	Chem Pharm Bull 16 1784 (1968) (1°, 2° alkyl; 1° benzylic)
	Ph ₃ PF ₂	Chem Pharm Bull 16 1009, 1784 (1968) (both 1°, 2° alkyl)
	Et ₂ NCF ₂ CHClF	J Gen Chem USSR 29 2125 (1959) (1° alkyl)
		TL 1065 (2° alkyl), 1249 (1°, 2° alkyl) (1962); 31 4309 (2° allylic), 7403 (2° alkyl) (1990)
		JOC 29 2187 (1964) (1°, 2° alkyl); 44 3406 (1979) (2° alkyl); 55 5291 (1990) (1° alkyl)
		Coll Czech Chem Commun 39 2616 (1974) (1° alkyl)
		Helv 58 2469 (1975) (1° allylic)
	Et ₂ NCF ₂ CHFCF ₃	BCSJ 52 3377 (1979) (1°, 2°, 3° alkyl)
		J Fluorine Chem 38 243 (1988) (1° benzylic)
		JOC 55 5291 (1990) (1° alkyl)
	Me ₂ C=CFNMe ₂	TL 30 3077 (1989) (1° alkyl; 1°, 3° allylic)
Cl	HCl	Org Syn Coll Vol 1 286, 288, 519 (1932) (all 1° alkyl)
		Org Syn Coll Vol 1 144 (1941) (3° alkyl)
		JACS 78 653 (1956) (1° benzylic)
		BSCF 632 (1974) (3° allylic, rearrangement)
		JOC 47 2590 (1982) (2° benzylic)
	aq HCl (phase transfer)	Syn 37 (1974) (1° alkyl)
	HCl, ZnCl ₂	Helv 20 1462 (1937) (1° alkyl)
		Org Syn Coll Vol 1 142 (1941) (1° alkyl)
		JCS 636 (1943) (1°, 2°, 3° alkyl)
	HCl, CaCl ₂ , CuCl, Cu	JOC 26 725 (1961) (3° propargylic)
	py·(HF) _n , NaCl	JOC 44 3872 (1979) (1°, 2°, 3° alkyl; 1° benzylic)
	(COCl) ₂ , DMF	JACS 107 3285 (1985) (1° alkyl)
	AcCl	JACS 63 1892 (1941); 108 3762 (1986)
		JOC 58 3748 (1993) (all 3° benzylic)
	H ₂ C=CHOCOCI	TL 28 2933 (1987) (1° benzylic)
	Cl ₃ COCO ₂ CCl ₃ , py	JOC 56 7186 (1991) (1° allylic)
	(CF ₃ CO) ₂ O/LiCl	Syn 511 (1987) (1° alkyl)
	Ph ₃ P·Cl ₂	JACS 86 964 (1964) (1°, 2° 3° alkyl)
		TL 30 6741 (1989) (1° benzylic)
		JOC 54 1459 (1989) (2° allylic)
	Ph ₃ P, NCS	Carbohydr Res 24 45 (1972) (1° alkyl)

- TL 3937 (1973) (2° alkyl); 32 5919 (1991) (1° alkyl)
- JACS 106 3286 (1984) (1° benzylic); 112 6942 (1990) (1° allylic)
- Ph₃P, Cl₃CCOCCl₃ JOC 44 359 (1979) (1°, 2°, 3° allylic); 46 824 (1981) (1°, 2° alkyl; 1°, 3° allylic); 57 5058 (1992) (1° allylic)
- Ph₃P, CCl₄ Chem Ind 900 (1966) (1°, 2° alkyl; 1° benzylic)
Angew Int 14 801 (1975) (review)
Can J Chem 44 1331 (1966) (1°, 2° alkyl)
Tetr 23 359 (1967) (1°, 2° alkyl)
CC 1358 (1968) (1°, 2° alkyl)
JOC 37 1466 (1972) (1°, 2° allylic); 43 1150 (2° alkyl), 2821 (mechanism) (1978); 51 5291 (1986) (1° alkyl); 57 3078 (1992) (1° allylic)
JACS 96 3684 (1974); 98 5016 (1976); 108 1019 (1986) (all 1° allylic)
BSCF 607 (1975) (2° allylic)
Org Syn Coll Vol 6 634 (1988) (1° allylic)
TL 30 6741 (1989) (1° benzylic)
- Ph₃P, CCl₄, py Carbohydr Res 61 511 (1978) (1° alkyl)
TL 32 3977 (1991) (1° > 2° alkyl)
- Ph₃P, Cl₃CCCl₃ Syn 139 (1983) (2° alkyl)
JOC 48 3721 (1983) (1° alkyl)
- polymer-PAr₂, CCl₄ CC 622 (1975) (1° alkyl)
JOC 40 1669 (1975) (1°, 2° alkyl; 1° benzylic); 48 3721 (1983) (1°, 2° alkyl; 1° allylic; 1° benzylic)
- polymer-PAr₂, Cl₃CCCl₃ JOC 48 3721 (1983) (1° alkyl)
-  CH₂CH₂PPh₂
CCl₄, HCCl₃ JOC 52 4999 (1987) (1°, 2° alkyl)
- (PhO)₃P, HCl JCS 2224 (1953) (1°, 2°, alkyl; 1° allylic)
(PhO)₃P, Cl₂ JCS 2281 (1954) (1°, 2°, 3° alkyl)
(PhO)₃P, NCS TL 3937 (1973) (2° alkyl, 1° benzylic)
(PhO)₃P, CCl₄ JCS 2224 (1953) (1° alkyl)
(PhO)₃P, C₆H₅CH₂Cl JCS 2224 (1953) (1°, 2° alkyl; 1° allylic)
JOC 30 2635 (1965) (2° alkyl)
- (n-C₈H₁₇)₃P, CCl₄ Can J Chem 46 86 (1968) (1°, 2° alkyl; 1° benzylic)
- (Me₂N)₃P, CCl₄ CC 1350 (1968) (1° alkyl)
BSCF 607 (1975) (2° allylic)
- PCl₃, DMF Syn 398 (1976) (1°, 2° alkyl; 1° allylic)
PCl₅ JCS 1138 (1946); 1709 (1953) (both 2° alkyl)
JCS C 1124 (1970) (2° alkyl)
Austral J Chem 29 133 (1976) (3° alkyl, retention)
JOC 27 1449 (1962) (1° alkyl)
- POCl₃ Syn 746 (1980) (1°, 2°, 3° alkyl; 1° benzylic)
POCl₃, DMF and other amides CL 923 (1978) (1°, 2° alkyl)
Me₂NPOCl₂



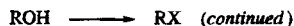
X	Reagent(s)	
Cl (<i>continued</i>)	 SOCl ₂	Z Chem 22 126 (1982) (1°, 2° alkyl; 1° benzylic) JACS 51 3475 (1929) (1° benzylic); 62 2295 (1940) (1° benzylic); 73 2239 (1951) (1° alkyl); 75 2053 (1953) (1° alkyl, 1° benzylic); 77 4182 (1955) (1°, 2° allylic); 107 3950 (1985) (1° alkyl); 111 989 (1989) (2° allylic); 112 6959 (1990) (1° benzylic) Ann 479 211 (1930) (1°, 2° allylic) JCS 684 (1942) (1° benzylic); 636 (1943) (1°, 2° alkyl); 1138 (1946) (2° alkyl); 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic); 2720 (1959) (2° allylic) Org Syn Coll Vol 4 333 (1963) (1° alkyl) JCS C 1124 (1970) (2° alkyl) TL 2931 (1970) (2° alkyl); 87 (1971) (1° alkyl); 36 4221 (1995) (2°, 3° allylic; rearrangement) BSCF 632 (1974) (3° allylic, rearrangement) JOC 52 547 (1987); 53 5552 (1988); 60 4666 (1995) (all 1° alkyl) TL 4339 (1972) (1°, 2° allylic; 1°, 2° benzylic); 3857 (1976) (1° allylic) Tetr 32 1675 (1976) (1° allylic) JOC 51 3098 (1986); 59 4853 (1994); 60 4617 (1995) (all 1° allylic) Org Syn Coll Vol 8 616 (1993) (1° allylic) JOC 36 3044 (1971) (1°, 2° allylic); 51 838 (1986) (2° allylic); 52 3860, 3883 (1987) (both 1° allylic); 53 1616 (1988) (1° allylic); 58 3692 (1993) (1° allylic) TL 28 723 (1987) (1° allylic) Compt Rend C 276 683 (1973) (1° allylic) TL 393 (1984) (1° allylic) CC 590 (1986) (1° allylic) TL 27 1907 (1986) (2° cyclopropylcarbinyl allylic); 36 7011 (1995) (1° alkyl) JOC 60 2638 (1995) (1°, 3° alkyl) SL 723 (1994) (2°, 3° alkyl; 1°, 2° benzylic; 1°, 2° allylic) JOC 53 3634 (1988) (1°, 2°, 3° alkyl; 1°, 3° allylic; 1°, 3° benzylic) SL 723 (1994) (1° allylic, 1° benzylic, 2° alkyl) BCSJ 54 1456 (1981) (1° allylic) TL 4575 (1978) (2° alkyl) JOC 49 3027 (1984) (1°, 2° alkyl; 1° allylic) Syn Commun 16 611 (1986) (2° alkyl)
	NCS, Me ₂ S	
	MsCl, LiCl, 2,6-lutidine or <i>s</i> -collidine	
	TsCl, py, Δ	
	TsCl, DMAP	
	Me ₃ SiCl	
	Me ₃ SiCl, DMSO	
	Me ₃ SiCl, cat BiCl ₃	
	Me ₃ SiCl, cat SeO ₂	
	Me ₃ SiCl ₃ , cat BiCl ₃	
	TiCl ₄ , PhNHMe	
	PdCl ₂ (PhCN) ₂	
	ZnCl ₂ , PPh ₃	
	EtO ₂ CN=NCO ₂ Et	

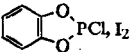
$\text{Me}_2\text{C}=\text{CClNMe}_2$	TL 30 3077 (1989) (1°, 2° alkyl; 1°, 2° allylic; 1°, 2° propargylic)
$(\text{Me}_2\text{N}^+=\text{CHCl})\text{Cl}^-$	TL 165 (1969); 33 4901 (1922) JOC 34 2163 (1969) (all 1° alkyl)
	CL 383 (1977) (1°, 2° alkyl)
	CL 619 (1976) (1°, 2° alkyl)
Br	
HBr	Helv 20 1462 (1937) (1° alkyl) JCS 636 (1943) (1°, 2° alkyl) Org Syn Coll Vol 2 246 (1943); 3 227 (1955) (both 1° alkyl) JOC 50 2759 (1985) (3° alkyl); 52 5560 (1987) (1°, 2° benzylic; 2° allylic) IACS 109 3098 (1987) (1° benzylic) TL 28 1223 (1987) (1°, 2° alkyl) TL 34 3741 (1993) (1° alkyl) Org Syn Coll Vol 1 25-35 (1941) (1° alkyl) JCS 636 (1943) (1° alkyl); 132 (1953) (1°, 2° alkyl) JOC 58 898 (1993) (1° alkyl) BCSJ 53 1181 (1980) (3° alkyl) JOC 44 3872 (1979) (1°, 2°, 3° alkyl; 1° benzylic) JACS 48 1080 (1926) (1°, 2° alkyl); 51 280 (1929) (1°, 2°, 3° alkyl); 62 2295 (1940) (2° alkyl); 68 2513 (1946) (2°, 3° alkyl); 82 410 (1960) (2° alkyl); 93 7016 (1971) (1° allylic); 98 4925 (1976) (1° allylic); 107 2712 (1985) (1° allylic); 111 5044 (1989) (3° allylic, rearrangement) JCS 636 (1943) (1°, 2° alkyl); 2005 (1952) (1° propargylic) Org Syn Coll Vol 2 358 (1943); 3 370 (1955) (both 1° alkyl) Helv 29 1133 (1946) (3° allylic, rearrangement) JOC 26 3645 (1961) (2° alkyl); 39 2135 (1974) (1° allylic); 52 4047 (1° allylic), 5594 (1° alkyl) (1987)
HBr (phase transfer) HBr, HOAc HBr, H ₂ SO ₄	
HBr, LiBr or CaBr ₂ [C ₅ H ₅ NH]F(HF) _x , NH ₄ Br PBr ₃	
PBr ₃ , py	Ann 479 211 (1930) (1°, 2° allylic) JACS 70 3314 (1948) (1° alkyl); 71 1292 (1949) (1° propargylic); 76 803 (1954) (1° alkyl) JCS 3650 (1950) (1° alkyl) Org Syn Coll Vol 3 793 (1955) (1° alkyl) JOC 41 1262 (1976) (3° allylic, rearrangement) JACS 93 7016 (1971); 99 3513 (1977) TL 3857 (1976) (all 1° allylic)
PBr ₃ , CaH ₂	

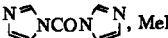
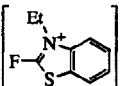


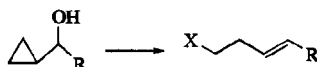
X	Reagent(s)	
Br (<i>continued</i>)	PBr ₅	JCS 1709 (1953) (2° alkyl) JOC 26 3645 (1971) (2° alkyl) Org Syn Coll Vol I 36 (1941) (1°, 2°, 3° alkyl)
	Br ₂ , P	JOC 53 6126 (1988) (1°, 2° alkyl)
	Br ₂ , Ph ₂ PCl, imidazole	JOC 53 6126 (1988) (1°, 2° alkyl)
	Br ₂ , <i>p</i> -Me ₂ NC ₆ H ₄ PPh ₂ , imidazole	JOC 53 6126 (1988) (1°, 2° alkyl)
	Br ₂ , polymer-PPh ₂ , imidazole	JOC 53 6126 (1988) (1°, 2° alkyl)
	Br ₂ , Ph ₃ P	Ann 626 26 (1959) (1°, 2° alkyl) JACS 86 964 (1964) (1°, 2° alkyl); 99 1612 (1977) (1° alkyl); 107 5238 (1985) (1°, 2° alkyl) JOC 30 2635, 2639, 3469 (1965) (all 2° alkyl); 58 502 (1993) (3° alkyl) TL 341 (1965) (2° alkyl) Syn 901 (1981) (1° allylic)
	Br ₂ , dppe	TL 28 767 (1987) (1° allylic, 1° propargylic) JACS 115 10400 (1993); 117 5958 (1995) (both 2° alkyl) JOC 60 1806 (1995) (1° allylic)
	Br ₂ , <i>n</i> -Bu ₃ P	JACS 86 964 (1964) (1°, 2° alkyl)
	Br ₂ , (PhO) ₃ P	JCS 2281 (1954) (1°, 2°, 3° alkyl) TL 483 (1963) (1°, 2° alkyl) JCS C 2260 (1967) (1°, 2° propargylic and allenic)
	C ₆ H ₅ CH ₂ Br, (PhO) ₃ P	JCS 2224 (1953) (1° alkyl, 1° allylic)
	NBS, (PhO) ₃ P	TL 3937 (1973) (2° alkyl)
	NBS, Ph ₃ P	JCS 2337 (1962) (1° alkyl) JOC 34 212 (1969); 51 2637 (1986); 60 1891 (1995) (all 1° alkyl) Carbohydr Res 24 45 (1972) (1° alkyl) TL 3937 (1973) (2° alkyl) JACS 99 3167 (1977) (1° alkyl); 107 7515 (1985) (1° allylic); 108 1035 (1986) (1° alkyl); 111 1861 (1989) (1° alkyl); 117 12683 (1995) (1° alkyl)
	NBA, Ph ₃ P	TL 3937 (1973) (2° alkyl)
	CBr ₄ , Ph ₃ P	JACS 92 2139 (1970) (1° allylic); 95 8749 (1973) (1° alkyl); 109 2738 (1987) (1° benzylic); 113 4252 (1991) (1° alkyl) JOC 42 353 (1977) (1° alkyl); 51 5291 (1986) (1° alkyl) TL 28 675 (1° allylic), 3225 (2° allylic), 6425 (1° alkyl) (1987) Carbohydr Res 61 511 (1978) (1° alkyl) TL 32 3977 (1991) (1° > 2° alkyl) JOC 51 789 (1986) (1° allylic) Can J Chem 46 86 (1968) (1° alkyl, 1° benzylic) CL 85 (1986) (1° allylic) TL 27 1607 (1986) (1° allylic)
	CBr ₄ , Ph ₃ P, py	
	CBr ₄ , dppe	
	CBr ₄ , (<i>n</i> -C ₈ H ₁₇) ₃ P	

$\text{BrCCl}_2\text{CCl}_2\text{Br}$, Ph_3P	Syn 139 (1983) (1°, 2° alkyl) TL 28 5751 (1987) (1° allylic)
Br_3CCBr_3 , Ph_3P	Syn 139 (1983) (2° alkyl)
2,4,5-tribromoimidazole, Ph_3P	JCS Perkin I 681 (1982) (1°, 2° alkyl)
Ph_3P , $\text{O}=\text{N}(\text{Me})\text{C}(\text{N}=\text{N})\text{O}/\text{MeBr}$	BCSJ 57 2675 (1984) (1°, 2° alkyl)
SOBr_2	JOC 26 3645 (1961) (2° alkyl); 53 72 (1988) (1° benzylic) TL 87 (1971) (1° alkyl); 36 4221 (1995) (2°, 3° allylic; rearrangement)
Me_2S , NBS	TL 4339 (1972) (1°, 2° allylic; 1°, 2° benzylic) JACS 108 1019 (1986) (1° allylic)
BH_3 , Br_2	Chem Ind 223 (1965) (?)
NaBH_4 , Br_2	Chem Ind 223 (1965) (?)
BBr_3	TL 35 1051 (1994) (3° > 2° alkyl)
Me_3SiBr	TL 4483 (1978) (1°, 2°, 3° alkyl; 1° benzylic); 36 7011 (1995) (1° alkyl)
Me_3SiCl , LiBr	JOC 45 1638 (1980) (1°, 2°, 3° alkyl; 1° allylic; 1°, 2° benzylic)
$(\text{Me}_3\text{Si})_2$, $\text{py} \cdot \text{HBr}_3$	JOC 45 1638 (1980) (1°, 2° alkyl; 1° allylic; 1°, 2° benzylic)
TiBr_4 , PhNHMe	BCSJ 54 1456 (1981) (1° allylic)
ZnBr_2 , Ph_3P	JOC 49 3027 (1984) (1° alkyl, 1° allylic); 52 2960 (1° alkyl), 4191 (1° alkyl) (1987)
$\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$	Syn 511 (1987) (1° alkyl, 1° allylic)
$(\text{CF}_3\text{CO})_2\text{O}/\text{LiBr}$	TL 28 4745 (1987) (1° allylic) CC 656 (1980) (2° alkyl)
PhSeCN , $n\text{-Bu}_3\text{P}/\text{Br}_2$, Et_3N	TL 30 3077 (1989) (1°, 2° alkyl; 1° allylic)
$\text{Me}_2\text{C}=\text{CBrNMe}_2$	Chem Pharm Bull 31 4189 (1983) (1°, 2° alkyl; 1° allylic; 1° benzylic)
$\text{N} \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{array} \text{CON} \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{array}$, PhCH_2Br or $\text{H}_2\text{C}=\text{CHCH}_2\text{Br}$	
$\left[\begin{array}{c} \text{Et} \\ \\ \text{F}-\text{N}^+-\text{S} \end{array} \begin{array}{c} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{array} \right] \text{BF}_4^-$, $\text{Et}_3\text{N}/\text{LiBr}$	CL 619 (1976) (1°, 2° alkyl)
I	
HI	Helv 20 1462 (1937) (1° alkyl) JCS 636 (1943) (1°, 2° alkyl)
HI, LiI or CaI_2	BCSJ 53 1181 (1980) (3° alkyl)
KI, H_3PO_4	JOC 15 491 (1950) (1°, 2°, 3° alkyl) Org Syn Coll Vol 4 323 (1963) (1° alkyl)
$\text{py} \cdot (\text{HF})_n$, KI	JOC 44 3872 (1979) (1°, 2°, 3° alkyl; 1° benzylic) TL 28 4969 (1987) (1° benzylic)
NaI, $\text{BF}_3 \cdot \text{OEt}_2$	SL 489 (1993) (1°, 2° alkyl)
KI, SOCl_2, DMF	TL 36 609 (1995) (2°, 3° alkyl; 1°, 2°, 3° benzylic)
I_2	Org Syn Coll Vol 2 322, 399 (1943) (both 1° alkyl)
P, I_2	TL 1801 (1979) (1°, 2°, 3° alkyl; 3° benzylic)
P_2L_4	Tetr 48 3735 (1992) (1° alkyl)



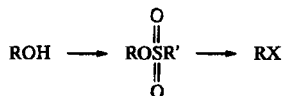
X	Reagent(s)	
I (continued)	Ph ₂ PCl, I ₂ , imidazole	JOC 53 6126 (1988) (1°, 2° alkyl); 60 3074 (1995) (1° alkyl) TL 34 2993 (1993) (2° allylic, S _N 2')
	Ph ₃ P, I ₂	JACS 86 964 (?), 2093 (1° alkyl) (1964)
	polymer-PPh ₂ ·I ₂	TL 36 167 (1995) (1° alkyl)
	R ₃ P·I ₂ (R = <i>n</i> -Bu, Ph), HMPA	Austral J Chem 35 517 (1982) (1°, 2° alkyl; 1° propargylic; 1° allylic)
	Ph ₃ P, I ₂ , imidazole	CC 978 (1979) (1°, 2° alkyl) JCS Perkin I 2866 (1980); 681 (1982) (both 1°, 2° alkyl) TL 24 4883 (1983) (1° propargylic); 28 3091 (1° alkyl), 5391 (1° alkyl), 5457 (1° alkyl) (1987) JOC 51 858 (1° alkyl), 4726 (1° alkyl) (1986); 54 3240 (1989) (2° alkyl) JACS 109 1186, 4717, 6187 (1987) (all 1° alkyl) CC 877 (1987) (1° alkyl) Syn Commun 20 1473 (1990) (1°, 2° alkyl) JOC 53 6126 (1988) (1°, 2° alkyl)
	<i>p</i> -Me ₂ NC ₆ H ₄ PPh ₂ , I ₂ , imidazole	
	polymer-PPh ₂ , I ₂ , imidazole	JOC 53 6126 (1988) (1°, 2° alkyl)
	Ph ₃ P, 2,4,5-triiodoimidazole	CC 978 (1979) (1°, 2° alkyl) JCS Perkin I 2866 (1980) (1°, 2° alkyl); 681 (1982) (1° alkyl)
	Ph ₃ P, NIS	Carbohydr Res 24 45 (1972) (1° alkyl) TL 3937 (1973) (2° alkyl)
	Ph ₃ P, ICH ₂ CH ₂ I	Syn 139 (1983) (1°, 2° alkyl)
	Ph ₃ P, Cl ₄ , py	Carbohydr Res 61 511 (1978) (1° alkyl) TL 32 3977 (1991) (1° > 2° alkyl)
	Ph ₃ P, ZnI ₂ , EtO ₂ CN=NC ₂ Et	JOC 49 3027 (1984) (1° alkyl) Syn Commun 16 611 (1986) (2° alkyl) TL 28 2977 (1987); 30 1637 (1989) (both 1° alkyl)
	Ph ₃ P, O=C(N=N)C(=O)Me	BCSJ 57 2675 (1984) (1°, 2° alkyl)
	(PhO) ₃ P, I ₂	JCS 2281 (1954) (1°, 2° alkyl)
	(PhO) ₃ P, CH ₃ I	JCS 2224 (1°, 2°, 3° alkyl; 1° allylic; 1°, 2° benzylic), 3002 (1° alkyl) (1953) JACS 86 2093 (1964); 88 5684 (1966) (both 1° alkyl) Austral J Chem 21 513 (1968) (2° alkyl) JOC 35 2319 (1° alkyl), 2868 (2° alkyl) (1970); 53 5046 (1988) (1° alkyl) Org Syn 51 44 (1971) (1° alkyl) TL 28 3123 (1987) (1° alkyl) Org Syn Coll Vol 6 830 (1988) (1°, 2° alkyl)
		JOC 32 4160 (1967) (1°, 2° alkyl)

(Me ₂ N) ₃ P·I ₂ , HMPA	Austral J Chem 35 517 (1982) (1° allylic)
BH ₃ , I ₂	Chem Ind 1582 (1964) (1°, 2° alkyl; 1° benzylic)
PhNEt ₂ ·BH ₃ , I ₂	TL 30 5663 (1989) (1°, 2°, 3° alkyl)
NaBH ₄ , I ₂	Chem Ind 223 (1965) (?)
Me ₃ SiCl ₃ , NaI	JOC 48 3667 (1983) (2°, 3° alkyl; 1° benzylic)
(Me ₃ Si) ₂ O·P ₂ O ₅ , NaI	Syn 460 (1983) (1°, 2° alkyl)
Me ₃ SiI	TL 2659 (1977) (1°, 2°, 3° alkyl; 1° benzylic); 36 7011 (1995) (1° alkyl)
Me ₃ SiSiMe ₃ , I ₂	Angew Int 18 612 (1979) (1°, 2° alkyl; 1° benzylic)
Me ₃ SiCl, NaI	JOC 44 1247 (1979) (1°, 2°, 3° alkyl; 1° allylic; 1° benzylic)
MgI ₂	TL 28 5063 (1987) (2° alkyl) TL 28 6441 (1987) (3° alkyl)
(CF ₃ CO) ₂ O/LiI	Syn 608 (1984) (2° allylic, rearrangement)
Me ₂ C=CINMe ₂	Syn 511 (1987) (1° alkyl)
 MeI	TL 30 3077 (1989) (1°, 2° alkyl; 1° allylic; 1° propargylic; 1° benzylic)
 BF ₄ ⁻ , Et ₃ N/LiI	Chem Pharm Bull 31 4189 (1983) (1°, 2° alkyl)
[C ₇ N(Me)=C=NCy]I	CL 619 (1976) (1°, 2° alkyl)
	Angew Int 11 229 (1972) (1°, 2° alkyl)



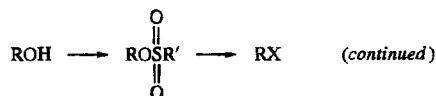
See page 291, Section 41.


2. Via Sulfonates



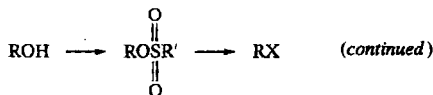
R' = CH₃, C₆H₅, *p*-C₆H₄CH₃, CF₃, *n*-C₄F₉

X	Reagent(s)	
F	KF (phase transfer)	Syn 428 (1974) (1°, 2° alkyl); 430 (1975) (2° alkyl)
	KF, CH ₃ OH	JACS 80 5559 (1958) (1° alkyl)
	KF, HOCH ₂ CH ₂ OH	JCS 872 (1958) (1° alkyl)
		Chem Ind 157 (1958) (1°, 2° alkyl)
		SL 55 (1995) (2° alkyl)
	KF, O(CH ₂ CH ₂ OH) ₂	JACS 77 4899 (1955) (1°, 2° alkyl)
		Can J Chem 34 757 (1956) (1° alkyl)



<u>X</u>	<u>Reagent(s)</u>	
F (continued)	KF, dicyclohexyl-18-crown-6	CC 879 (1974) (1° alkyl)
	KF, 18-crown-6	TL 2023 (1979) (2° alkyl)
	KF, HCONH ₂	TL 34 293 (1993) (2° alpha to ester)
	CsF	JACS 110 8686 (1988) (2° benzylic)
		TL 35 1851 (1994) (2° benzylic)
	AgF, py	JOC 53 5046 (1988) (1° alkyl)
	<i>n</i> -Bu ₄ NF (no solvent)	JOC 49 3216 (1984) (1°, 2° alkyl)
	<i>n</i> -Bu ₄ NF, solvent?	TL 28 4003 (1987) (2° alkyl)
	<i>n</i> -Bu ₄ NF, Et ₂ O	JACS 109 3046 (1987) (1° alkyl)
	<i>n</i> -Bu ₄ NF, THF	JOC 44 2194 (1979) (2° alkyl)
		SL 676 (1992) (2° alkyl)
	<i>n</i> -Bu ₄ NF, CH ₃ COCH ₃ or CH ₃ COCH ₂ CH ₃	JCS 954 (1962) (2° alkyl)
	<i>n</i> -Bu ₄ NF, CH ₃ CN	Carbohydr Res 5 292 (1967) (1°, 2° alkyl)
		Can J Chem 59 396 (1981) (1°, 2° alkyl)
	<i>n</i> -Bu ₄ NF·3H ₂ O; <i>o</i> -C ₆ H ₄ Cl ₂ , CH ₃ CN or THF (resin-NMe ₃)F	JOC 52 658 (1987) (1° alkyl); 58 6843 (1993) (1° alkyl)
		Syn 472 (1976) (1°, 2° alkyl)
		JCS Perkin I 2248 (1979) (1°, 2° alkyl)
	Et ₃ N·3HF, Et ₃ N (<i>n</i> -Bu ₄ N)HF ₂	TL 31 6527 (1990) (2° alkyl)
	(<i>n</i> -Bu ₄ N)Ph ₃ SiF ₂	TL 28 4733 (1987) (1°, 2° alkyl)
	(<i>n</i> -Bu ₃ MeP)F	JACS 117 5166 (1995) (1°, 2° alkyl)
Cl		TL 353 (1979) (2° alkyl)
		JOC 44 3406 (1979) (2° alkyl)
		Tetr 36 1931 (1980) (1° alkyl)
	[(Me ₂ N) ₃ S]Me ₃ SiF ₂	JACS 106 5348 (1984) (1° alkyl)
	<i>n</i> -C ₄ F ₉ SO ₂ F, DBU	TL 36 2611 (1995) (1°, 2° alkyl)
	polymer-H _n F _{n+1} (<i>n</i> = 0, 1, 2)	JOC 54 5380 (1989) (2° alkyl)
	LiCl, ROH (CH ₃ COCH ₂ CH ₃)	JCS 315 (2° alkyl), 326 (1° alkyl) (1949); 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic); 954 (1962) (2° alkyl)
	LiCl, HMPA	TL 1393 (1969) (1° allylic)
		JOC 44 2369 (1970) (1° alkyl)
		JACS 99 1612 (1977) (1° allylic)
		Org Syn Coll Vol 6 638 (1988) (1° allylic)
	LiCl, CH ₃ CONEt ₂	
		JOC 44 2369 (1970) (1° alkyl)
	LiCl, DMF	JOC 51 5291 (1986) (1° alkyl)
	LiCl, DMF, collidine	Tetr 27 5979 (1971) (1° allylic)
		JOC 36 3044 (1971) (1°, 2° allylic)
		BSCF 607 (1975) (1° allylic)

	LiCl, CH ₃ COCH ₂ COCH ₃	JOC 54 1432 (1989) (2° alkyl)
	NaCl or KCl, dicyclohexyl-18-crown-6	CC 879 (1974) (1° alkyl)
	KCl (phase transfer)	Syn 430 (1975) (2° alkyl)
	CaCl ₂ , DMSO	JOC 58 272 (1993) (1° allylic, 1° benzylic)
	<i>n</i> -Bu ₄ NCl, CH ₂ Cl ₂	JACS 115 9305 (1993) (2° alkyl)
	<i>n</i> -Bu ₄ NCl, CH ₃ COCH ₂ CH ₃	JCS 954 (1962) (2° alkyl)
	(resin-NMe ₃)Cl	JCS Perkin I 2248 (1979) (2° alkyl)
	py·HCl	Monatsh 83 1398 (1952) (1° alkyl)
		JACS 80 2726 (1958) (1° alkyl)
		JOC 26 2883 (1961) (2° alkyl)
	TsCl, py, Δ (direct)	Compt Rend C 276 683 (1973) (1° allylic)
	AlCl ₃	TL 30 4555 (1989) (2° alkyl)
Br	HBr	JOC 27 4349 (1962) (1° alkyl)
	LiBr, THF	JOC 48 2270 (1983) (1° alkyl)
		JACS 107 2712 (1985) (1° allylic); 110 8117 (1988) (1° alkyl)
	LiBr, CH ₃ COCH ₃	JCS 954 (1962) (2° alkyl)
		JOC 35 2803 (1970) (1° alkyl); 52 2337 (1987) (1° alkyl)
		JACS 107 2730 (1985) (1° allylic); 109 6937 (1987) (1° alkyl)
	LiBr, CH ₃ COCH ₂ COCH ₃	JOC 54 1432 (1989) (2° alkyl)
	LiBr, CH ₃ CONEt ₂	JOC 44 2369 (1979) (1° alkyl)
	LiBr, CH ₃ CN	JOC 58 771 (1993) (2° alkyl)
	NaBr	JOC 26 3645 (1961) (2° alkyl)
		Org Syn Coll Vol 4 753 (1963) (1° alkyl)
	NaBr, dicyclohexyl-18-crown-6	CC 879 (1974) (1° alkyl)
	KBr (phase transfer)	Syn 430 (1975) (2° alkyl)
	KBr, dicyclohexyl-18-crown-6	CC 879 (1974) (1°, 2° alkyl)
	CaBr ₂	JCS 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic)
		JOC 27 624 (1962) (2° alkyl); 58 272 (1993) (1° allylic, 1° benzylic); 58 272 (1993) (1° allylic)
	MgBr ₂	J Lipid Res 7 568 (1966) (1° alkyl)
	<i>n</i> -Bu ₄ NBr, C ₆ H ₆	JOC 45 4387 (1980) (1°, 2° alkyl)
	<i>n</i> -Bu ₄ NBr, toluene	JACS 117 197 (1995) (1° alkyl)
	<i>n</i> -Bu ₄ NBr, THF	JOC 53 1922 (1988) (1° alkyl)
	<i>n</i> -Bu ₄ NBr, CH ₃ COCH ₂ CH ₃	JCS 954 (1962) (2° alkyl)
I	<i>n</i> -Bu ₄ NBr, HMPA	JACS 107 3271 (1985) (1° alkyl)
	py·HBr	Monatsh 83 1398 (1952) (1° alkyl)
I	NaI	JCS 315 (2° alkyl), 326 (1°, 2° alkyl), 2542 (1° alkyl) (1949); 3650 (1950) (1° alkyl); 2005 (1952) (1° propargylic); 955 (1962) (2° alkyl)
		JACS 72 561 (1950); 83 1460 (1961); 91 4771 (1969) (all 1° alkyl); 107 2124 (1° propargylic), 7967 (1° alkyl) (1985); 108 468 (1986) (1° alkyl)

XReagent(s)

I (continued)

NaI (continued)

JOC 21 1487 (1956) (1° alkyl); 52 4517 (1° alkyl); 4810 (1° propargylic) (1987); 54 1432 (1989) (2° alkyl)
 Can J Chem 34 757 (1956) (1° alkyl)
 TL 35 3909 (1994) (2° alkyl)
 JACS 107 196 (1985) (1° alkyl)
 CC 879 (1974) (1° alkyl)
 Monatsh 82 970 (1951) (1°, 2° alkyl)
 Syn 430 (1975) (2° alkyl)
 JOC 58 272 (1993) (1° allylic)
 JOC 53 1922 (1988) (1° alkyl)
 JACS 115 10174 (1993) (2° alkyl)
 JOC 45 4387 (1980) (1°, 2° alkyl)
 TL 28 2941 (1987) (1° alkyl)
 Monatsh 83 1398 (1952) (1° alkyl)
 JACS 109 4717 (1987) (1° allylic)

NaI, copper bronze

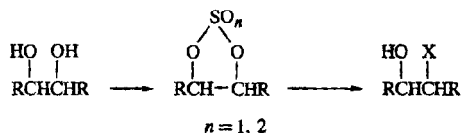
NaI or KI, dicyclohexyl-18-crown-6

KI

KI (phase transfer)

CaI₂n-Bu₄NI, THFn-Bu₄NI, C₆H₆

py·HI

ZnI₂

See page 972, Section 3.

3. Via Haloformates

XYReagent

F

F

BF₃·OEt₂

JACS 77 5033 (1955)

Cl

F

TIF

JACS 77 3099 (1955)

Cl

BF₃·OEt₂

JACS 77 5033 (1955)

NaCl

JOC 32 2633 (1967)

PPh₃

Ann 698 106 (1966)

Br

NaBr

JOC 32 2633 (1967)

I

NaI

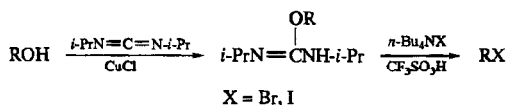
JOC 32 2633 (1967)

4. Other Approaches

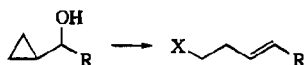
For approaches via silyl ethers, see page 685, Section 7.



<u>X</u>	<u>Reagent(s)</u>	
F	Ph ₂ NCN, KO- <i>t</i> -Bu/HF or HBF ₄ /Δ	Can J Chem 43 3173 (1965)
Cl	2,6-(NO ₂) ₂ C ₆ H ₃ F/LiCl NaH/CS ₂ /MeI/SO ₂ Cl ₂	BSCF 405 (1975) TL 29 3053 (1988) (retention)
I	ClCO ₂ CHClCH ₃ /NaI, Δ	TL 26 5445 (1985)



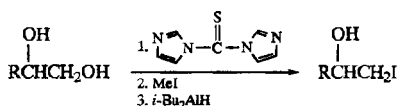
TL 28 4445 (1987)



See page 291, Section 41.

5. Diols

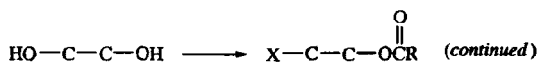
See also page 697, Section 2.



TL 36 7367 (1995)



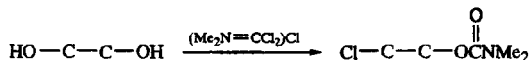
<u>X</u>	<u>R</u>	<u>Reagent(s)</u>	
Cl	Me	CH ₃ C(OMe) ₃ , Me ₃ SiCl AcOCMe ₂ COCl AcOC(Me)(Et)COCl AcOCHMeCOCl <i>o</i> -AcOC ₆ H ₄ COCl, HOAc	Tetr 48 10515 (1992) JCS 1918 (1964) JACS 95 4016, 4025 (1973) JCS 1918, 4840 (1964) JCS 1918 (1964) TL 1475 (1973) Syn 533 (1976); 142 (1984)
	<i>i</i> -Pr	<i>i</i> -PrCO ₂ C(Me)(Et)COCl	JCS 1918 (1964)
	Ph	PhCO ₂ C(Me)(Et)COCl	JCS 4840 (1964)



<u>X</u>	<u>R</u>	<u>Reagent(s)</u>	
Br	Me	HBr, HOAc	JCS Perkin I 1214 (1973)
			JOC 56 2869 (1991)
		CH ₃ C(OMe) ₃ / AcBr	Tetr 48 10515 (1992)
		AcOCMe ₂ COBr	JACS 95 4025 (1973)
	Ph	AcOC(Me)(Et)COBr	TL 25 367 (1984)
		<i>o</i> -AcOC ₆ H ₄ COBr, HOAc	JCS 4840 (1964)
		PhCHO / NBS	Syn 142 (1984)
		PhC(OMe) ₃ / AcBr	See page 727, Section 2.
I	Me	CH ₃ C(OMe) ₃ / NaI, AcCl	JOC 59 5799 (1994)
			Tetr 48 10515 (1992)

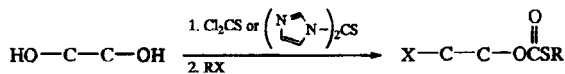


<u>X</u>	<u>R</u>	<u>Reagent(s)</u>	
Cl	Me	AcOC(Me)(Et)COCl	JCS 4840 (1964)
Br	Ph	PhCHO / NBS	See page 727, Section 2.



Austral J Chem 35 2257 (1982)

TL 27 4697 (1986)



X = Cl, Br, I

JOC 34 3011 (1969)

TL 3793 (1973)

JCS Perkin I 1773 (1975)

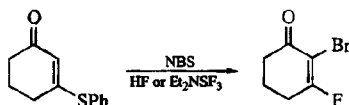
9. HALOGENATION OF PHENOLS

For ring halogenation, see page 619, Section 2.

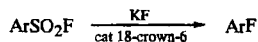
	$\text{ArOH} \longrightarrow \text{ArX}$	
<u>X</u>	<u>Reagent(s)</u>	
Cl	POCl_3	JCS 678 (1944) IACS 76 6073 (1954) Org Syn Coll Vol 3 272 (1955) JOC 27 1462 (1962)
	$\text{POCl}_3, \text{PCl}_5$	JACS 76 1109 (1954) JCS 1666 (1964)
	PCl_5	JCS 1666 (1964)
	$\text{PCl}_5, \text{C}_6\text{H}_5\text{COCl}$	JCS 1666 (1964)
	PhPCl_4	JOC 55 3415 (1990)
	$\text{COCl}_2, \text{Ph}_3\text{P}$	Ann 698 106 (1966)
Br	$\text{Ph}_3\text{P}, \text{Br}_2$	IACS 86 964 (1964) Org Syn Coll Vol 8 57 (1993)
$\text{ArOH} \xrightarrow{\text{CF}_3\text{SO}_2\text{Cl}} \text{ArOTf} \xrightarrow[\text{DMF}]{\text{NaI}} \text{ArI}$		
J Med Chem 33 758 (1990)		

10. HALOGENATION OF SULFUR AND SELENIUM COMPOUNDS

or the halogenation of α -nitro sulfones, see page 677, Section 6.



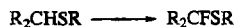
TL 35 85 (1994)



JOC 53 4398 (1988)



Syn 371 (1981)



Et_2NSF_3 , cat SbCl_3

JOC 58 3800 (1993)

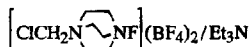
$\text{Et}_3\text{N} \cdot 3\text{HF}$, electrolysis

JOC 55 6074 (1990); 58 4200 (1993); 59 5937 (1994); 60 3459, 7654 (1995)

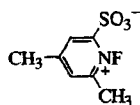
TL 31 2287 (1990); 35 7245 (1994); 36 3851 (1995)
CC 1027 (1991)

$(n\text{-Bu}_4\text{N})\text{H}_2\text{F}_3$, 1,3-dibromo-5,5-dimethylhydantoin

TL 36 8243 (1995)



JOC 58 2791 (1993)



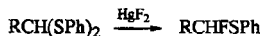
JOC 60 6563 (1995)



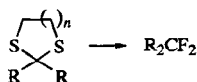
Et_2NSF_3	TL 31 5609 (1990)
$\text{Et}_2\text{NSF}_3, \text{SbCl}_5$	TL 31 5609 (1990)
	JOC 55 4757 (1990)
$\text{Et}_2\text{NSF}_3, \text{cat ZnI}_2$	JACS 107 735 (1985)

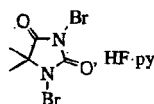


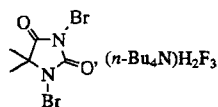
X	Reagent(s)	
Cl	Cl_2, py	BCSJ 43 2271 (1970)
	NCS	Int J Sulfur Chem 8 1 (1973)
	NCS, base	BCSJ 44 1726 (1971)
	NCS, silica gel	Syn 831 (1986)
	$\text{SO}_2\text{Cl}_2, \text{py}$	BCSJ 43 2271 (1970)
		Syn 89 (1971)
	$\text{PhICl}_2, \text{py}$	CC 607 (1969)
		JCS Perkin I 1883 (1972)
	<i>t</i> -BuOCl, KOAc or py	TL 5259 (1969)
	TsCl, py	JACS 90 4496 (1968)
Br	NOCl, py	TL 5415 (1968)
	Br_2, py	Syn 588 (1970)
	$\text{Br}_2, \text{AgNO}_3, \text{py}$	JCS Perkin I 1883 (1972)
		JACS 95 7431 (1973)
	NBS, py	Syn 588 (1970)
		JCS Perkin I 1883 (1972)
	NBS, cat <i>p</i> -TsOH	Int J Sulfur Chem 8 1 (1973)



TL 28 3901 (1987)



Reagent(s)	<i>n</i>	
SO_2ClF or $\text{SO}_2\text{Cl}_2, \text{py} \cdot (\text{HF})_n$ (R = Ar)	2	SL 691 (1993)
ArIF_2 (R = Ar)	1, 2	SL 191 (1991)
		JOC 59 7190 (1994)
	1	JOC 51 3508 (1986)


 $(n\text{-Bu}_4\text{N})\text{H}_2\text{F}_3$

1, 2

SL 909 (1991)

 NBS, $(n\text{-Bu}_4\text{N})\text{H}_2\text{F}_3$

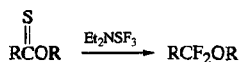
1, 2

SL 909 (1991)

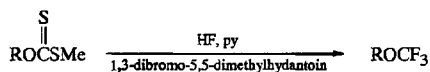
 NIS, $(n\text{-Bu}_4\text{N})\text{H}_2\text{F}_3$

1, 2

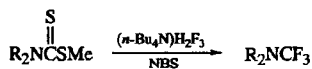
SL 909 (1991)



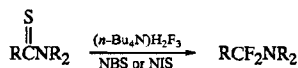
JOC 55 768 (1990)



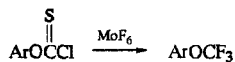
TL 33 4173 (1992)



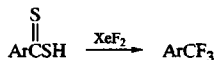
TL 33 4177 (1992)



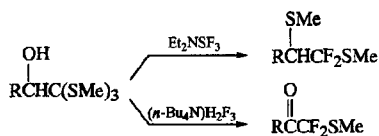
TL 35 3983 (1994)



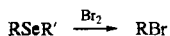
TL 2253 (1973)



TL 31 3357 (1990)



TL 36 6121 (1995)

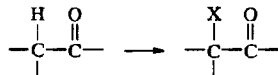


TL 2647 (1976)

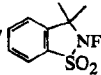
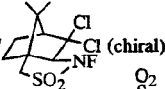
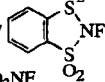
11. HALOGENATION OF CARBONYL AND RELATED COMPOUNDS

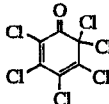
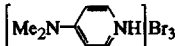
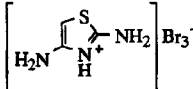
1. Aldehydes and Ketones

See also page 619, Section 2.



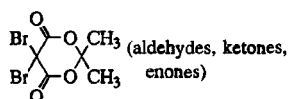
Review: H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., Menlo Park, California (1972), pp 459-478

<u>X</u>	<u>Reagent(s)</u>	
F	base / $\text{CH}_3\text{CO}_2\text{F}$ base / $\text{RSO}_2\text{NFR}'$	Syn 665 (1985) JACS 106 452 (1984) TL 29 6087 (1988) (chiral)
	base / 	TL 32 1779 (mono- and difluorination), 3819 (1991)
	base /  (chiral)	TL 34 3971 (1993)
	$\text{NaN}(\text{SiMe}_3)_2$ /  LDA / $(\text{PhSO}_2)_2\text{NF}$ LDA / $(\text{CF}_3\text{SO}_2)_2\text{NF}$	TL 32 1631 (1991) JOC 60 4730 (1995) SL 187 (1991) JOC 56 4925 (1991)
Cl	Cl_2	JCS 3869 (1953) Org Syn Coll Vol 3 188 (1955)

X	Reagent(s)	
Cl (continued)	Cl ₂ (continued)	<p>Helv 40 274 (1957) JACS 81 1201 (1959) JOC 46 2532 (1981); 60 4153 (1995) Ber 122 523 (1989) Ann 672 103 (1964) Org Syn Coll Vol 4 162 (1963) JOC 29 1956 (1964); 37 4090 (1972); 46 4486 (1981); 60 2714 (1995) Syn Commun 11 7 (1981) JACS 77 5274 (1955) CC 1336 (1986) Syn 545 (1988); 212 (1990) CC 1278 (1980) JOC 59 2613 (1994) JOC 51 3380 (1986) JACS 107 7771 (1985) JACS 113 4037 (1991); 114 9419 (1992) TL 33 3571 (1992)</p>
	Cl ₂ , hv	
	Cl ₂ , cat I ₂	
	SO ₂ Cl ₂ (ketones only)	
	CuCl ₂ ·2H ₂ O, LiCl, H ₂ O	
	TiCl ₃	
	(PhCH ₂ NMe ₃)ICl ₂	
	(polymer-C ₆ H ₄ CH ₂ NMe ₃)ICl ₂	
	NaClO ₃ , HCl	
	<i>t</i> -BuOCl, HOAc	
	LDA / CF ₃ SO ₂ Cl	
	LDA / NCS	
	NaN(SiMe ₃) ₂ / NCS	
	 (aryl ketones only)	Syn 1018 (1982)
Br	Br ₂ (ketones)	<p>Org Syn Coll Vol 1 127 (1941); 6 193 (1988) JACS 75 2301 (1953); 108 1251 (1986) BSCF 4169 (1969) JOC 58 5546 (1993); 59 6973 (1994) BSCF 1465 (1973) JCS Perkin I 501 (1977) JACS 72 362 (1950) JOC 35 186 (1970); 51 3380 (1986) JOC 48 2520 (1983) JOC 38 2576 (1973) JACS 70 417 (1948); 116 7658 (1994) TL 23 3405 (1982)</p>
	Br ₂ , dioxane (aldehydes)	
	Br ₂ , hv, cyclohexene oxide	
	Br ₂ , HOAc	
	Br ₂ , AlCl ₃	
	base / Br ₂	
	py·HBr ₃	
	 (pyrrolidone) ₃ ·HBr ₃	<p>Syn Commun 14 939 (1984) Can J Chem 47 706 (1969) JOC 52 5624 (1987)</p>
	 (PhNMe ₃)Br ₃	<p>Syn 488 (1980) TL (9) 24 (1959) BSCF 1822 (1961); 90 (1962) JACS 106 3539 (1984) JOC 52 4792 (1987)</p>

(polymer- $C_6H_4CH_2NMe_3$)Br₃[Ph₃P(CH₂)₂CO₂H]Br₃

NBS

NCCHBrCON(CH₃)₂ or BrCH(CN)₂NCCBr₂CON(CH₃)₂

PhSeBr

CuBr₂

Org Syn Coll Vol 6 175 (1988)

Syn 64 (1979); 143 (1980)

TL 373 (1975)

JACS 75 2301 (1953); 109 7230 (1987)

JOC 59 5774 (1994)

Syn 140 (1978)

JACS 107 7524 (1985)

JOC 55 1506 (1990)

Tetr 31 231 (1975)

Ind J Chem B 17 305 (1980)

JOC 51 3380 (1986)

JOC 26 765 (1961); 27 2937, 4397 (1962);
29 3459 (1964); 40 1990 (1975); 54
2190 (1989); 55 105 (1990); 60 554
(1995)

I

I₂, CaO or KOH

JACS 80 250 (1958); 81 439 (1959)

JOC 25 1966 (1960)

I₂, Cu(OAc)₂, HOAc, Δ

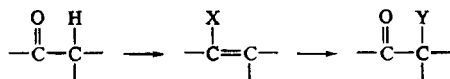
Syn 312 (1981)

base/I₂

TL 2817 (1979)

Me₃SiI, (Me₃Si)₂NH/NaI,

JOC 52 3919 (1987)

m-ClC₆H₄CO₂H

X

Y

Reagent(s)

OH

F

F₂

JOC 47 1107 (1982)

OR

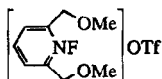
F

FCIO₃, py
CF₃OF

JACS 81 5259 (1959)

CC 804 (1968)

Israel J Chem 17 60 (1978)



JACS 112 8563 (1990)

Cl

NCS, NaOAc, H₂O
Cl⁻, Pb(OAc)₄
NH₄Cl, electrolysis

JOC 59 6955 (1994)

Syn 1021 (1982)

JOC 45 2731 (1980)

Br

Br₂
NBS, NaOAc, H₂O
Br⁻, Pb(OAc)₄
NH₄Br, electrolysis

BSCF 4169 (1969)

JOC 57 752 (1992)

Syn 1021 (1982)

JOC 45 2731 (1980)

Syn 1021 (1982)

I

I⁻, Pb(OAc)₄OBR₂

Cl

NCS

Can J Chem 50 2387 (1972)

Br

NBS

Can J Chem 50 2387 (1972)

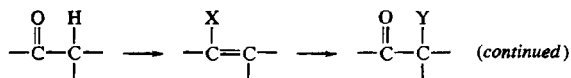
OSiR₃

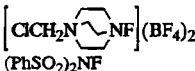

F

F₂

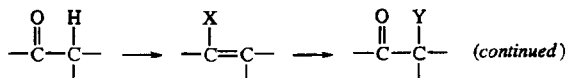
TL 27 2715 (1986)

JOC 53 5153 (1988)



X	Y	Reagent(s)	
OSiR ₃	F	CF ₃ OF	JACS 102 4845 (1980)
(continued)		(C ₃ H ₅ NF)OTf	JOC 53 5153 (1988)
			TL 27 4465 (1986)
			JACS 112 8563 (1990)
			JOC 57 1597 (1992)
			Org Syn Coll Vol 8 286 (1993)
			JOC 58 2791 (1993)
			SL 187 (1991)
			
		(PhSO ₂) ₂ NF	JOC 60 4730 (1995)
			
		CsSO ₄ F	JOC 53 5153 (1988)
		XeF ₂	JOC 53 5153 (1988)
Cl		Cl ₂	JOC 39 1785 (1974)
			Syn 194 (1976)
			TL 25 503 (1984)
		NCS	TL 27 2563 (1986)
			JOC 58 1501 (1993)
		Cl ⁻ , Pb(OAc) ₄	Syn 1021 (1982)
		MeLi/NCS	JACS 112 3466 (1990)
		SO ₂ Cl ₂	JOC 56 6764 (1991)
		FeCl ₃	JOC 45 2022 (1980)
		CuCl ₂	JOC 45 2022 (1980)
		1,3-dichloro-3,5-dimethyl-hydantoin	SL 891 (1991)
		NH ₄ Cl, electrolysis	JOC 45 2731 (1980)
Br		Br ₂	JACS 109 2435 (1987); 114 9419 (1992)
			JOC 56 6764 (1991)
		NBS	JOC 39 1785 (1974); 52 3346 (1987); 56 6764 (1991); 58 1501 (1993); 59 7709 (1994); 60 554 (1995)
			Syn 194 (1976)
			JACS 113 2071 (1991); 116 1776, 7658 (1994)
		NH ₄ Br, electrolysis	JOC 45 2731 (1980)
		Br ⁻ , Pb(OAc) ₄	Syn 1021 (1982)
I		I ₂ , PCC, molecular sieves	Syn Commun 12 1127 (1982)
		I ₂ , AgOAc/(Et ₃ NH)F	JOC 44 1731 (1979)
		I ₂ , Cu(NO ₃) ₂	JOC 56 6708 (1991)
		NaI, m-ClC ₆ H ₄ CO ₃ H/H ₃ O ⁺	JOC 52 3919 (1987)
			TL 31 3745 (1990)
		I ⁻ , Pb(OAc) ₄	Syn 1021 (1982)

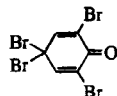
O ₂ CR	F	F ₂	JOC 53 5153 (1988)
		F ₂ , NaO ₂ CCF ₃	CC 479 (1979)
			JACS 101 2782 (1979)
			J Fluorine Chem 16 19 (1980)
		F ₂ , <i>n</i> -C ₇ F ₁₅ CO ₂ K	JOC 50 3698 (1985)
		CsSO ₄ F	JOC 53 5153 (1988)
		XeF ₂	JOC 53 5153 (1988)
		XeF ₂ , cat HF	JOC 47 573 (1982)
		CF ₃ OF	CC 804 (1968); 1497 (1969); 122 (1972)
			Israel J Chem 17 60 (1978)
	Cl	R ₂ OF	JOC 53 5153 (1988)
		CF ₂ (OF) ₂	CC 122 (1972)
		SF ₅ OF	CC 122 (1972)
		RCO ₂ F	CC 122 (1972)
			JOC 55 2621 (1990)
		$\left[\text{ClCH}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{NF} \right] (\text{BF}_4)_2$	JOC 58 2791 (1993)
		(C ₅ H ₅ NF)OTf	JACS 112 8563 (1990)
		C ₅ H ₅ NF(C ₅ H ₅ N)B ₂ F ₇	JOC 56 5962 (1991)
		MeLi/R ₂ SO ₂ NFR'	JACS 106 452 (1984)
		Cl ⁻ , Pb(OAc) ₄	Syn 1021 (1982)
Br	Br	NH ₄ Cl, electrolysis	JOC 45 2731 (1980)
		Br ₂	JACS 66 1325 (1994); 67 1430 (1945); 101 2782 (1979)
			Org Syn Coll Vol 3 127 (1955)
			JCS 907, 911 (1959); 1312, 3839 (1962); 2933 (1965)
			Tetr 21 273 (1965)
			JCS Perkin I 126 (1978)
		NBS	JACS 75 3513 (1953)
			JOC 59 6728 (1994)
		py·HBr ₃	JOC 59 1058 (1994)
		Br ⁻ , Pb(OAc) ₄	Syn 1021 (1982)
I	I	NH ₄ Br, electrolysis	JOC 45 2731 (1980)
		I ₂ , TiOAc	JCS Perkin I 126 (1978)
		I ₂ , Cu(OAc) ₂ , HOAc	Syn 312 (1981)
		I ₂ , Cu(NO ₃) ₂	JOC 56 6708 (1991)
		NIS	JACS 75 3493 (1953); 76 1722 (1954); 77 3826 (1955)
		I ⁻ , Pb(OAc) ₄	Syn 1021 (1982)
		NH ₄ I, electrolysis	JOC 45 2731 (1980)
NR ₂	F	FCIO ₃	JOC 23 1406 (1958)
		CF ₃ OF	CC 804 (1968)
			Israel J Chem 17 60 (1978)
		(C ₅ H ₅ NF)OTf	JACS 112 8563 (1990)
	Cl	Cl ₂	Acta Chem Scand B 32 646 (1978)
		Br ₂	Acta Chem Scand B 32 646 (1978)
		I	JOC 52 3919 (1987)
		NaI, <i>m</i> -ClC ₆ H ₄ CO ₃ H/H ₃ O ⁺	



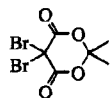
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
NHAc	F	FCIO ₃	JOC 27 702 (1962) J Med Chem 7 108 (1964) JOC 56 5962 (1991)
		C ₃ H ₅ NF(C ₃ H ₅ N)B ₂ F ₇	



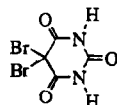
NBS, cat HClO ₄	Mendeleev Commun 159 (1995)
pyrrolidone·HBr ₃	Can J Chem 47 706 (1969)
(Ph ₃ PCH ₂ CH ₂ CO ₂ H)Br ₃	TL 373 (1975)
NCCHBrCONMe ₂	Tetr 31 231 (1975)



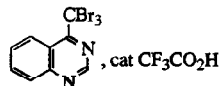
Tetr 29 1625 (1973)



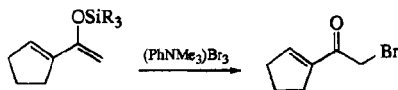
Syn 140 (1978)



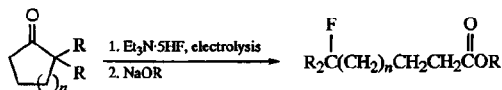
Ber 118 4288 (1985)



Gazz Chim Ital 117 83 (1987)



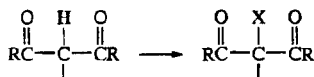
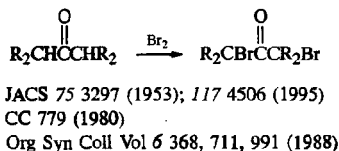
SL 651 (1994)


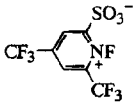
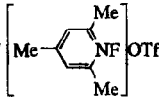
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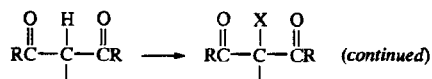
TL 36 6511 (1995)



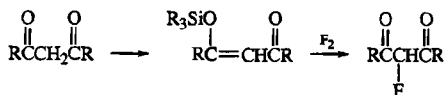
<u>X</u>	<u>Reagent(s)</u>	
Cl	Cl ₂	Org Syn Coll Vol 3 538 (1955)
	SO ₂ Cl ₂ , cat TsOH·2H ₂ O	JOC 53 3843 (1988)
	NCS, NaOAc, HOAc	JOC 53 4864 (1988)
Br	NBS	JOC 54 1435 (1989)
	(PhNMe ₃)Br ₃	Org Syn Coll Vol 6 175 (1988)



<u>X</u>	<u>Reagent(s)</u>	
F	F ₂	CC 21 (1995)
	NaH/CH ₃ CO ₂ F	JOC 48 724 (1983)
	(CF ₃ SO ₂) ₂ NF	JOC 56 4925 (1991); 57 4281 (1992); 60 4730 (1995)
		J Fluorine Chem 58 71 (1992)
		CC 179 (1991)
		CC 343 (1994)
		JOC 60 6563 (1995)
	base / 	JACS 112 8563 (1990)
Cl	XeF ₂ , cat HF	JOC 47 573 (1982)
	C ₁₉ XeF ₆	TL 277 (1980)
	CuCl ₂	JCS Perkin I 3171 (1993)
Br	CuCl ₂ , Mn(OAc) ₃	JCS Perkin I 3171 (1993)
	NaH/CuCl ₂	JOC 58 4596 (1993)
	Me ₃ SiCl, KBrO ₃	Bull Russ Acad Sci, Div Chem Sci 41 356 (1992)
Br	Br ₂	JACS 67 1145 (1945)
	Br ₂ , NaOAc	JACS 83 439 (1961)


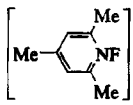


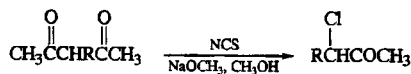
<u>X</u>	<u>Reagent(s)</u>	
Br (continued)	CuBr ₂	IOC 26 765 (1961) JCS Perkin I 3171 (1993)
	CuBr ₂ , Mn(OAc) ₃	JCS Perkin I 3171 (1993)
	NaH / CuBr ₂	IOC 58 4596 (1993)
I	H ₅ IO ₆	CC 11 (1970)



IOC 52 4307 (1987)



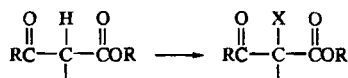
<u>X</u>	<u>Reagent(s)</u>	
F	XeF ₂ , cat HF	IOC 47 573 (1982)
	XeF ₂ , polymer- 	CC 759 (1980)
	 OTf, ZnCl ₂	JACS 112 8563 (1990)
	(CF ₃ SO ₂) ₂ NF	CC 179 (1991) J Fluorine Chem 58 71 (1992)
Cl	CF ₃ SO ₂ Cl, Et ₃ N	TL 3643 (1979)
Br	Br ₂	Org Syn Coll Vol 2 244 (1943) TL 28 6539 (1987)



TL 28 5505 (1987)



JOC USSR 23 2319 (1987)



X

F

Reagent(s)

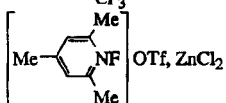
F_2 CC 21 (1995)
 $\text{C}_{10}\text{XeF}_6$ TL 21 277 (1980)
 $\text{KOEt}/\text{FCIO}_3$ Can J Chem 41 1833 (1963)
 $\text{CH}_3\text{CO}_2\text{F}$ JOC 48 724 (1983)
 $\text{base}/\text{CH}_3\text{CO}_2\text{F}$ JOC 48 724 (1983)

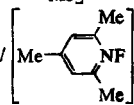
$\text{NaH}/$  J Fluorine Chem 52 389 (1991)

$[\text{ClCH}_2\text{N} \langle \text{ring} \rangle \text{NF}](\text{BF}_4)_2$ CC 343 (1994)

$\text{base}/[\text{ClCH}_2\text{N} \langle \text{ring} \rangle \text{NF}](\text{BF}_4)_2$ JOC 58 2781 (1993)

 JOC 60 6563 (1995)

 JACS 112 8563 (1990)

$\text{base}/$  TL 27 4465 (1986)
 JACS 112 8563 (1990)

$\text{base}/$  TL 29 6087 (1988) (chiral)

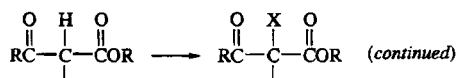
$\text{base}/$  TL 34 3971 (1993) (chiral)

$(\text{CF}_3\text{SO}_2)_2\text{NF}$ CC 179 (1991)
 JOC 56 4925 (1991); 57 4281 (1992); 60 4730 (1995)

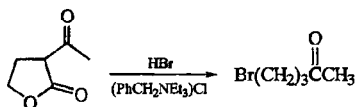
 J Fluorine Chem 58 71 (1992)
 JOC 60 4730 (1995)

Cl

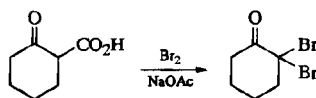
$\text{Cl}_2, \text{NaOAc} \cdot 3\text{H}_2\text{O}$ JCS 2539 (1959)
 SO_2Cl_2 JACS 66 1132 (1944)
 JCS 2898 (1949)
 Org Syn Coll Vol 4 590 (1963)
 JOC 29 2706 (1964)
 Syn 188 (1987); 595 (1990)



<u>X</u>	<u>Reagent(s)</u>	
Cl (<i>continued</i>)	Me ₃ SiCl, KBrO ₃	Bull Russ Acad Sci, Div Chem Sci 41 356 (1992)
	Na/TsCl	JACS 69 2932 (1947)
	NaOEt/TsCl	J Prakt Chem 65 528 (1902)
	NaH/CuCl ₂	JOC 58 4596 (1993)
Br	Br ₂	JACS 67 1145 (1945)
		JOC 15 572 (1950)
	NaH/Br ₂	TL 4067 (1972)
		Syn Commun 25 1045 (1995)
	NBS	Ber 92 2775 (1959)
	NBS, Et ₃ N	JOC 60 554 (1995)
	NaH/NBS	Syn Commun 25 1045 (1995)
	CuBr ₂ , PhI(OH)OTs	TL 36 7735 (1995)
	NaH/CuBr ₂	JOC 58 4596 (1993)



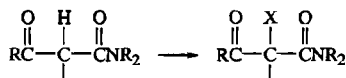
Syn Commun 10 897 (1980)



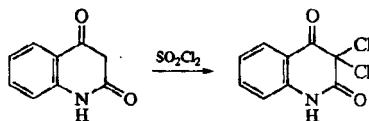
JACS 75 3297 (1953)



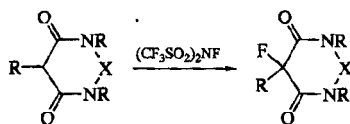
<u>X</u>	<u>Reagent</u>	
F	(CF ₃ SO ₂) ₂ NF	CC 179 (1991)
		J Fluorine Chem 58 71 (1992)
Cl	CF ₃ SO ₂ Cl, Et ₃ N	TL 3643 (1979)
		JACS 110 5533 (1988)
	SO ₂ Cl ₂	JOC 29 2706 (1964)
		Syn 188 (1987)



<u>X</u>	<u>Reagent(s)</u>	
F		JOC 60 4730 (1995)
	$\left[\text{ClCH}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \text{---} \end{array} \text{NF} \right] (\text{BF}_4)_2$	CC 343 (1994)
Cl	SO_2Cl_2 $\text{TsN}(\text{Cl})\text{Na}$ $\text{X}_3\text{CSO}_2\text{Cl}$ (X = F, Cl), Et_3N	Monatsh 123 617 (1992) CC 1151 (1986) Chem Pharm Bull 34 1553 (1986)
Br	Br_2 $\text{Br}_2, \text{Et}_3\text{N}$ NBS $\left[\text{Me}_2\text{N} \begin{array}{c} \diagup \diagdown \\ \text{---} \end{array} \text{NH} \right] \text{Br}_3$ $\text{Br}_2\text{C}(\text{CN})_2$, cat $\text{BF}_3 \cdot \text{OEt}_2$	Monatsh 123 617 (1992) Chem Pharm Bull 34 1553 (1986) CC 1151 (1986) Syn Commun 14 939 (1984) BCSJ 37 547 (1964)

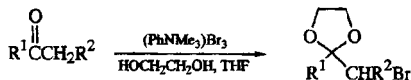


Monatsh 123 617 (1992)



X = —, CO

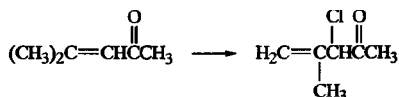
JOC 57 4281 (1992)



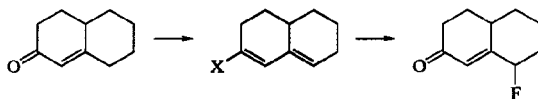
Syn 309 (1982)



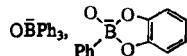
<u>X</u>	<u>Reagents</u>	
Cl, Br	PhSeX , py	TL 22 3301 (1981)
Br	$\text{Br}_2/\text{Et}_3\text{N}$	JOC 33 1454 (1968); 47 5088 (1982) JACS 112 775 (1990)



See page 614, Section 2.

X

MeO, AcO

Me₃SiO, AcOMe₃SiOReagentCF₃OF(PhSO₂)₂NF(C₅H₅NF)OTfC₅H₅NF(C₅H₅N)B₂F₇

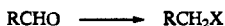
Israel J Chem 17 60 (1978)

TL 36 4721 (1995)

TL 27 4465 (1986)

JOC 56 5962 (1991)

JOC 60 6563 (1995)

X

F

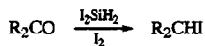
I

Reagent(s)PhSH, H⁺/HgF₂/Na, EtOHI₂, PhNEt₂·BH₃I₂SiH₂

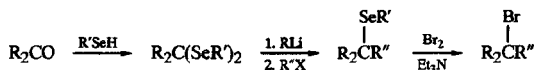
TL 29 6851 (1988)

TL 30 5663 (1989)

JOC 55 2927 (1990)



JOC 55 2927 (1990)



TL 2647 (1976)

X

F

Reagent(s)SF₄, (HF)

JACS 81 3165 (1959); 82 543 (1960); 89 88

(1967); 91 1386 (1969); 94 2020 (1972)

JOC 26 2436 (1961); 27 3164, 4086 (1962); 31

991 (1966); 36 818 (1971); 57 132 (1992); 58

6843 (1993)

J Med Chem 6 174 (1963)


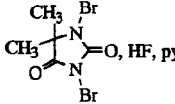
Tetr 20 1625 (1964)

Org Rxs 21 1 (1974) (review)

JOC USSR 17 1260 (1981)

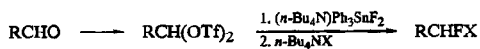
PhSF₃

JACS 84 3058 (1962); 91 1386 (1969)

	Et_2NSF_3	Syn 787 (1973) JOC 40 574 (1975); 45 2883 (1980); 55 1579 (1990); 58 6843 (1993); 59 2956 (1994); 60 5174 (1995) JCS Perkin I 1354 (1979) J Med Chem 22 971 (1979) JACS 109 3046 (1987) TL 29 5217 (1988); 36 2389 (1995) Org Rxs 35 513 (1988) (review) SL 55 (1995) Helv 58 2469 (1975)
		
	$\text{HSCH}_2\text{CH}_2\text{SH}$, $\text{BF}_3 \cdot 2\text{HOAc}$ / 	JOC 51 3508 (1986)
	SeF_4 XeF_2 , HF (ArCHO) MoF_6 , cat BF_3	JACS 96 925 (1974) SL 265 (1994) Tetr 27 3965 (1971); 31 391 (1975)
Cl	PCl_5	Ann 115 29 (1860); 196 259 (1879); 314 369 (1901); 401 121 (1913); 612 1 (1958); 1 (1980) Compt Rend 136 94 (1903) Ber 40 2160 (1907); 43 2940 (1910) JACS 50 172 (1928); 59 2434 (1937); 71 3439 (1949); 72 3952 (1950); 73 1007, 5382 (1951); 108 3762 (1986); 116 9019 (1994) Org Syn Coll Vol 2 573 (1943) JCS 1425 (1952); 3116 (1954) JOC 59 3798, 6223 (1994) Ann 435 190 (1924); 501 219 (1933) Org Syn Coll Vol 6 845 (1988) TL 33 683 (1992)
	PCl_5 , PCl_3	
	Ph_3P , CCl_4	
Br	PCl_3Br_2	Ber 7 759 (1874); 8 406 (1875) JCS 45 522 (1884) Ann 235 299 (1886) Rec Trav Chim 50 316, 837 (1931) Ann 341 15 (1905) Syn Commun 9 341 (1979)
	HBr (on PhCHO) BBr_3 (on ArCHO)	
I	$\text{H}_2\text{NNH}_2/\text{I}_2$, Et_3N	JCS 470 (1962) Austral J Chem 23 989 (1970) JOC 59 3798, 6223 (1994)
	$\text{Me}_2\text{NNH}_2/\text{H}_2\text{NNH}_2/\text{I}_2$, Et_3N	JOC 33 4317 (1968)

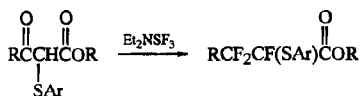


X	Reagent	
F	$(n\text{-Bu}_4\text{N})\text{Ph}_3\text{SnF}_2$	TL 33 7787 (1992)
I	MgI_2	TL 33 2043 (1992)

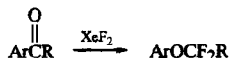


X = Cl, Br, I

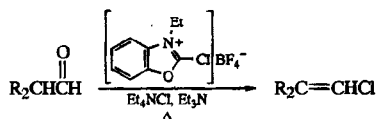
SL 587 (1993)



TL 36 5007 (1995)



JOC 55 1099 (1990)



CL 465 (1978)



X

Reagent(s)

F



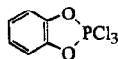
JOC 50 2007 (1985)

Cl

PCl₃
PCl₅

TL 32 827 (1991)
Ann 308 264 (1899); 1 (1980)
JACS 56 1207 (1934); 59 2434 (1937); 63
1175 (1941); 65 2208 (1943); 77 1691
(1955); 90 395 (1968); 109 7838 (1987)
Org Mag Res 10 192 (1977)
JOC 43 2839 (1978); 47 1084 (1982); 60
7015 (1995)
SL 279 (1991)
TL 31 6753 (1990)
JACS 65 2208 (1943)
TL 30 6221 (1989); 33 7635 (1992)
JOC 58 7732 (1993)
JOC 47 1397 (1982)

PCl₅, PCl₃
PCl₅, PCl₃, POCl₃
POCl₃
POCl₃, DMF
POCl₃, Et₃N



Z Chem 22 126 (1982)

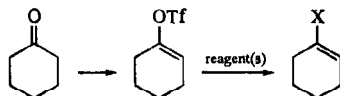
Br

PBr₃
POBr₃, Et₃N

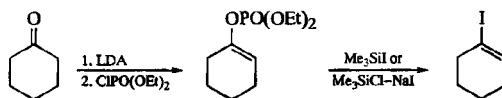
TL 32 827 (1991)
JACS 110 911 (1988)

I	N_2H_4/I_2 , Et_3N	JCS 470 (1962) JACS 91 2115 (1969); 103 6526 (1981); 104 6646 (1982) CC 174 (1969) JOC 34 3502 (1969); 53 4855 (1988) Austral J Chem 23 989 (1970); 24 1425 (1971) BCSJ 53 3252 (1980) JCS Perkin I 3017 (1982) JACS 103 7122 (1981) TL 24 1605 (1983); 27 1811 (1986); 29 2989 (1988) JOC 50 2438 (1985); 54 3334 (1989) JOC 58 4989 (1993) JOC 48 4058 (1983) TL 34 6559 (1993)
	N_2H_4/I_2 , piperidine	
	N_2H_4/I_2 , guanidine base	
	N_2H_4/I_2 , DBN	
	N_2H_4/I_2 , DABCO	

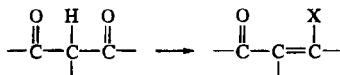
See also page 301, Section 54.2.



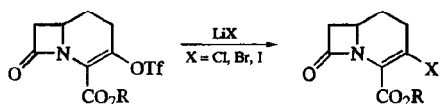
X	Reagent(s)	
Br	$Me_3SnSnMe_3$, cat $Pd(PPh_3)_4$ / Br_2 $(n-Bu_3Sn)_2Cu(CN)Li_2$ / Br_2	JOC 51 277 (1986) TL 29 4795 (1988)
I	MgI_2 , Et_3N	Syn 222 (1986)



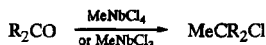
TL 34 2433 (1993)



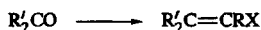
X	Reagent(s)	
Cl	PCl_3	JCS 83 110, 494 (1903); 1996 (1955); 2431 (1956) JACS 72 1645 (1950) Can J Chem 37 1870 (1959) J Gen Chem USSR 31 3719 (1961) JOC 30 1129 (1965) JCS Perkin II 142 (1972) J Gen Chem USSR 31 3719 (1961) JCS 83 110 (1903) Ann 672 158 (1958)
	PCl_5	
	$POCl_3$	



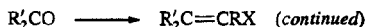
JOC 54 4962 (1989)



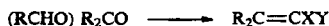
TL 31 503 (1990)



<u>X</u>	<u>Reagent(s)</u>	
F	$Ph_3P=CHF$ (R = H)	Syn 75 (1969) Ber 104 2885 (1971) JOC 40 2796 (1975)
	$Ph_3P=CHR / PhLi / FClO_3$	Syn 38 (1969)
	$[(n-Bu_3P)_2CF]Cl / NaOH$ (R = H)	JACS 107 2811 (1985); 109 3046 (1987)
	$PhSO_2\bar{C}FPO(OEt)_2 / n-Bu_3SnH / CsF, NH_3, MeOH$ (R = H)	JACS 113 7439 (1991)
	$PhSO_2\bar{C}FPO(OEt)_2 / Al(Hg)$ (R = H)	TL 31 5449 (1990)
	$PhSO(NMe)CHLiF / Al(Hg)$ (R = H)	TL 29 3365 (1988)
F, Cl	$ArSOC(Li)RX / MsCl / n-BuLi$	TL 33 1483 (1992)
F, Cl, Br, I	$(o-MeOCH_2OC_6H_4)_3P=CHX$ (Z selective, R = H)	TL 34 1925 (1993)
Cl	$Ph_3P=CHCl$ (R = H)	JACS 82 1510 (1960); 83 1617 (1961) Ber 94 1373 (1961); 99 689 (1966) CC 446 (1978) JOC 58 5802 (1993); 60 6571 (1995)
	$Ph_3P=CHR / n-BuLi$ or $PhLi / Cl_2IC_6H_5$	Syn 38 (1969) TL 447 (1970)
	$Ph_3P=CHR / n-BuLi / NCS$	TL 447 (1970)
	$HCCl_3, CrCl_2$ (R = H)	JACS 108 7408 (1986) JOC 56 1347 (1991)
Br	$Ph_3P=CHBr$ (R = H)	Angew Int 1 51 (1962) Ber 99 689 (1966) TL 21 4021 (1980) JACS 114 9836 (1992) JOC 57 651 (1992)
	$Ph_3P=CBrR$	JOC 43 2833 (1978); 60 2962 (1995) TL 27 1995 (1986)
	$Ph_3P=CHR / PhLi / Br_2$	Syn 38 (1969)
	$LiCHBr_2 / Zn, HOAc$ (R = H)	TL 22 3745 (1981) JOC 53 863 (1988)
	$HCBBr_3, CrBr_3, LiAlH_4$ (R = H)	JACS 108 7408 (1986)
I	$Ph_3P=CHI$ (R = H)	TL 30 2173, 5261 (1989) JACS 112 5875 (1990) JOC 58 2381 (1993); 60 7849 (1995)



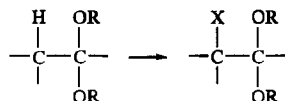
<u>X</u>	<u>Reagent(s)</u>	
I (continued)	Ph ₃ P=CRl	TL 35 2827 (1994)
	Ph ₃ P=CHR/ <i>n</i> -BuLi/Hg(OAc) ₂ /I ₂	TL 447 (1970)
	HCl ₃ , CrCl ₂ (R = H)	JACS 108 7408 (1986); 114 2260 (1992); 115 2268, 4497 (1993); 117 6224 (1995)
		TL 30 2911 (1989); 31 307 (1990); 34 6559 (1993)
		JOC 58 2381 (1993)



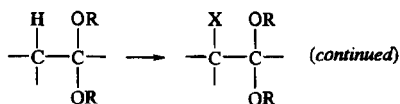
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
F	F	NaO ₂ CCF ₂ Cl, PPh ₃	TL 1461 (1964) JOC 30 1027 (1965); 32 1311 (1967); 33 1854 (1968); 53 1775 (1988)
		NaO ₂ CCF ₂ Cl, <i>n</i> -Bu ₃ P	JOC 30 2543 (1965)
		X ₂ CF ₂ (X = Cl, Br), (Me ₂ N) ₃ P	Syn Commun 3 197 (1973)
		Br ₂ CF ₂ , PPh ₃	JACS 112 6439 (1990)
		Ph ₂ P(O)CF ₂ Li	J Fluorine Chem 1 123 (1971-72)
		PhSO ₂ CF ₂ Li/MeCl/SmI ₂	TL 31 5571 (1990)
		NaO ₂ CCFCl ₂ , PPh ₃	TL 33 3101 (1992)
	Cl		TL 71 (1968)
		HCFCI ₂ , KO- <i>t</i> -Bu, PPh ₃	JOC 35 2125 (1970)
			JACS 84 854 (1962)
			TL 71 (1968)
	Br	CFBr ₃ , PPh ₃	J Fluorine Chem 1 381 (1971-72)
			JACS 115 5430 (1993)
	I	PhSO ₂ CFPO(OEt) ₂ / <i>n</i> -Bu ₃ SnH/I ₂	JACS 114 360 (1992)
	CO ₂ H	RO ₂ CCOCHFPCO ₂ R, base/ KOH	Compt Rend 250 1073 (1960)
	CO ₂ R	(EtO) ₂ POCFLiCO ₂ R	JCS 4033 (1961)
			Ann 674 1 (1964)
			J Med Chem 25 71 (1982)
			BSCF 448, 783 (1985)
			JACS 115 7103 (1993)
			JOC 58 5683 (1993); 59 1210 (1994)
			SL 729 (1994)
		FCI ₂ CCO ₂ R, Zn-Cu, Ac ₂ O	CL 1145 (1987)
			JACS 115 7103 (1993)
		ClCH(CO ₂ R) ₂ , KF, sulfolane	CL 1259 (1981)
		FCH ₂ CO ₂ R, NaH	BSCF 1569 (1967)
		RO ₂ CCOCHFPCO ₂ R, base	JCS 5261 (1960)
			JCS C 1232 (1968)
			TL 34 6903 (1993)
	SO ₂ Ph	PhSO ₂ CFPO(OEt) ₂	JOC 59 8034 (1994)

Cl	Cl	CCl ₄ , PPh ₃	JACS 84 1312 (1962)
		XCCl ₃ (X = Cl, Br), PPh ₃ , CH ₃ CN	Compt Rend C 276 903 (1973)
		CCl ₄ , PPh ₃ , Mg	TL 29 3003 (1988)
		CCl ₄ , P(NMe ₂) ₃	TL 33 683 (1992)
		BrCCl ₃ , P(NMe ₂) ₃	BSCF 2047 (1971)
		HCCl ₃ , KO- <i>t</i> -Bu, PPh ₃	TL 1035 (1971)
		LiCCl ₂ PO(OEt) ₂	TL 1239 (1977); 28 5473 (1987)
			JACS 84 854 (1962)
			JOMC 59 237 (1973)
			Syn 458 (1975)
Br	Br	LiCCl ₂ SiMe ₃	JOC 60 5588 (1995)
		CClBr ₃ , PPh ₃	TL 24 4727 (1983)
			JACS 115 5430 (1993)
			JACS 84 1745 (1962); 115 5430 (1993)
			BSCF 3145 (1972)
			Compt Rend C 274 1357 (1972)
			TL 3769 (1972); 1373 (1975); 28 5145 (1987)
			JOC 60 5588 (1995)
		CBr ₄ , PPh ₃ , Et ₃ N	TL 35 3529 (1994)
		CBr ₄ , PPh ₃ , Zn	TL 3769 (1972)
I	I	CBr ₄ , P(NMe ₂) ₃	TL 1035 (1971)
		HCCBr ₃ , KO- <i>t</i> -Bu, PPh ₃	JACS 84 854 (1962)
		Cl ₄ , PPh ₃ (RCHO only)	CC 296 (1985)
		I ₂ CHPO(OEt) ₂ , base	J Chem Res (S) 330 (1986)
			Syn 1071 (1993)

2. Acetals



X	Reagent(s)	
Cl	Cl ₂	BSCF 2735 (1973)
	SO ₂ Cl ₂	JOC 55 5400 (1990)
Br	Br ₂	BSCF 4169 (1969); 2735 (1973)
		JOC 38 3250 (1973); 55 5400 (1990); 57 2765 (1992)
	Br ₂ , hv	Ber 95 803 (1962)
	Br ₂ , 2-methoxynaphthalene	JOC 52 3018 (1987) (chiral)
	Br ₂ , py	JACS 64 1963 (1942)
	Br ₂ , CaCO ₃	JACS 49 2517 (1927); 64 1966 (1942)
		JOC 58 2501 (1993)
	Br ₂ , cat HBr	Angew 25 259 (1986)

XReagent(s)

Br (continued)

Br₂, (HBr), electrolysis
(PhNMe₃)Br₃

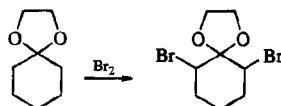
Syn Commun 10 821 (1980)
 BSCF 1822 (1961)
 Tetr 19 861 (1963)
 JOC 54 4951 (1989); 55 202 (1990)
 JOC 57 2765 (1992)
 JACS 84 2344 (1962)
 JOC 57 2765 (1992)
 JOC 57 2765 (1992)
 JACS 73 973 (1951)
 Ber 95 803 (1962)

(R₄N)Br₃
py·HBr₃(R₄P)Br₃
NBS, hν
NBS, (PhCO₂)₂

I

ICl

JOC 55 5400 (1990)



JACS 110 8500 (1988)
 JOC 59 5700, 5708 (1994)

XYReagent(s)

OR

Cl
Br

BCl₃
 Me₂BBr
 Me₃SiBr
 Me₃SiI

TL 28 5595 (1987)
 JOC 49 3912 (1984)
 Ber 113 3058 (1980)
 Ber 113 3075 (1980)
 Carbohydr Res 115 95 (1983)

I

Me₃SiCl, NaI

Ann 1052 (1984)

O₂CRBr
I

Me₃SiBr
 Me₃SiI
 Me₃SiCl, NaI

Ber 113 3075 (1980)
 Ber 113 3075 (1980)
 Ann 1052 (1984)

SPh

F

Et₂NSF₃, NBS
 HF·py, NBS

JACS 106 4189 (1984)
 JACS 106 4189 (1984)

XReagent(s)

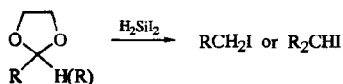
Br

LiBr, BF₃·OEt₂
 LiBr, Me₃SiCl

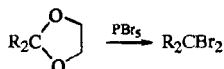
TL 32 1081 (1991)
 TL 32 1081 (1991)

CBr_4 , PPh_3	TL 30 557 (1989)
$\text{Ph}_3\text{P}\cdot\text{Br}_2$	JOC 40 2410 (1975); 44 4603 (1979); 56 3102 (1991)
	Syn Commun 6 21 (1976)
	JACS 101 4773 (1979); 107 686 (1985)
$\text{dppe}\cdot 2\text{Br}_2$	TL 28 767 (1987)
	JACS 112 4078 (1990); 114 3926 (1992)
	SL 444 (1992)
	JOC 58 165, 3516 (1993)
NaI , $\text{BF}_3\cdot\text{OEt}_2$	TL 32 1081 (1991)
NaI , Me_3SiCl	TL 32 1081 (1991)
dppe , I_2	TL 28 767 (1987)

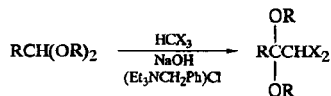
I



JOC 50 2927 (1990)



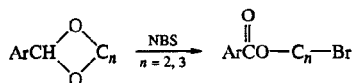
JACS 108 1265 (1986)

 $\text{X} = \text{Cl, Br}$

TL 1103 (1978)

Ber 112 2402 (1979)

J Chem Res (S) 94, 95 (1980)



Carbohydr Res 2 86 (1966); 50 35 (1976); 63 77 (1978)

CC 716 (1966)

JOC 34 1035, 1045, 1053 (1969); 35 225 (1970); 59 5317, 5799 (1994); 60 3600 (1995)

Methods Carbohydr Chem 6 183 (1972)

Chem Pharm Bull 23 1283 (1975)

Can J Chem 55 1348 (1977)

TL 4999 (1978)

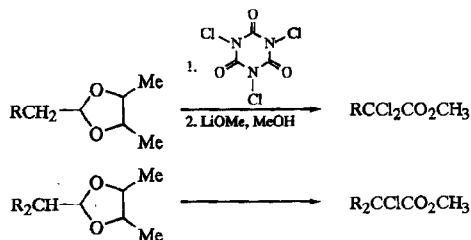
Syn 503 (1985); 811 (1986)

JACS 114 4453 (1992)

Org Syn Coll Vol 8 363 (1993)

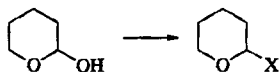


JACS 117 7862 (1995)



TL 35 2961 (1994)

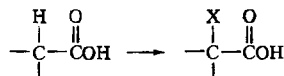
3. Lactols



Reagent(s)

X	Et_2NSF_3	TL 26 3, 5 (1985)
F	$\left[\text{C}_6\text{H}_4\text{NMe}^+ \text{OTs}^- \right]$	CL 935 (1983)
	$(\text{Et}_3\text{O})\text{BF}_4, \text{PPh}_3,$	Helv 68 283 (1985)
	$\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$	Carbohydr Res 127 C5 (1984)
	$\text{CF}_3\text{CHFCF}_2\text{NEt}_2$	
Cl	SOCl_2	TL 21 1421 (1980)
Br	PBr_3	TL 21 1421 (1980)
F, Cl, Br, I	$\text{Me}_2\text{C}=\text{CXNR}_2$	TL 30 3081 (1989)

4. Carboxylic Acids

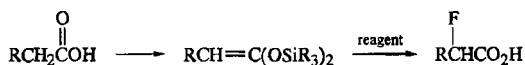


Review: Chem Rev 52 237 (1953)

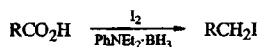
Reagent(s)

X	$n\text{-BuLi} / \text{ArSO}_2\text{NFR}'$	JACS 106 452 (1984)
F	$\text{Cl}_2, \text{O}_2, \text{ClSO}_3\text{H}, (\text{chloranil})$	JOC 40 2960 (1975)
Cl		Chem Ind 538 (1977)
		BCSJ 52 255 (1979)

		Org Syn 59 20 (1980)
		Org Syn Coll Vol 6 90 (1988)
	Cl ₂ ; ClSO ₃ H; 7,7,8,8-tetra- cyanoquinodimethane	JOC 48 1364 (1983)
	SO ₂ Cl ₂	JACS 69 86 (1947)
	SOCl ₂ , hv	JOC 38 3919 (1973)
	LDA/CCl ₄	JOC 52 307 (1987)
Br	Br ₂ , P, (H ₂ O)/H ₂ O	Ber 14 891 (1881); 20 2026 (1887); 22 1745 (1889); 24 938, 2388 (1891) Ann 242 141 (1887) Org Syn Coll Vol 2 74 (1943)
	Br ₂ , PCl ₃	JACS 71 2581 (1949) Org Syn Coll Vol 6 403 (1988)
I	I ₂ , Cu(OAc) ₂ , HOAc	CL 1509 (1984)
	I ₂ , CuCl, CuCl ₂	CL 1509 (1984)

Reagent

F ₂	JOC 55 3423 (1990)
CF ₃ OF	JACS 102 4845 (1980)

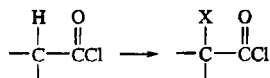


TL 30 5663 (1989)



JACS 82 543 (1960)
JOC USSR 13 2000 (1977)
JOC 58 6843 (1993); 59 3821 (1994)

5. Acid Halides

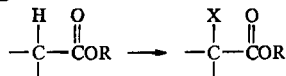


<u>X</u>	<u>Reagent(s)</u>	
Cl	NCS, SOCl ₂	JOC 40 3420 (1975)
Br	Br ₂	JOC 55 2950 (1990); 56 7328 (1991) Org Syn Coll Vol 6 190 (1988)
	NBS, HBr	JOC 40 3420 (1975)
	NBS, SOCl ₂	
I	I ₂ , SOCl ₂	JOC 40 3420 (1975)

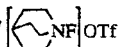


JOC 29 1 (1964)

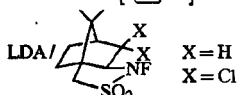
6. Esters and Lactones

XReagent(s)

F

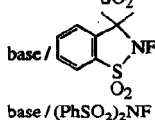
KN(SiMe₃)₂ /  OTf

TL 32 3815 (1991)



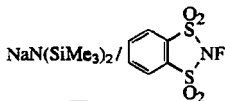
TL 29 6087 (1988) (chiral)

TL 34 3971 (1993) (chiral)

TL 32 1779 (mono- and difluorination),
3815 (1991)base / (PhSO₂)₂NF

TL 32 3815 (1991)

SL 187 (1991)



TL 32 1631 (1991)

JOC 60 4730 (1995)

LDA / (CF₃SO₂)₂NF

JOC 56 4925 (1991)

KN(SiMe₃)₂ / XeF₂

TL 32 3815 (1991)

Et₃N·3HF, electrolysis

TL 31 3137 (1990)

Cl

Cl₂, PCl₅

JACS 66 2074 (1944)

LDA / CCl₄

JOC 43 3687 (1978)

TL 32 4623 (1991)

Br

P, Br₂

Org Syn Coll Vol 5 255 (1973) (lactone)

P, Br₂ / ROH

Syn 39 (1969)

LDA / BrCH₂CH₂Br

JOC 54 1468 (1989) (lactone)

LDA / CBr₄

JOC 43 3687 (1978)

JACS 116 3125 (1994)

LiN(SiMe₃)₂ / CBr₄

TL 32 3569 (1991)

LiNR₂ / Br₂

TL 3995 (1971)

JOC 43 3687 (1978)

I

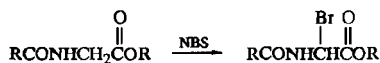
LiNR₂ / I₂

TL 3995 (1971); 28 2477 (1987)

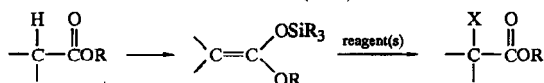
LDA / ZnCl₂ / I₂


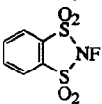
JOC 43 3687 (1991)

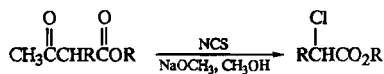
JOC 52 4414 (1987)



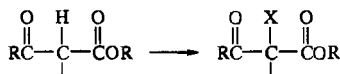
TL 29 1565 (1988)



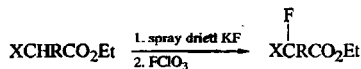
<u>X</u>	<u>Reagent(s)</u>	
F	F ₂	JOC 55 3423 (1990)
	CF ₃ OF	JACS 102 4845 (1980)
	 OTf	TL 27 4465 (1986)
		JACS 112 8563 (1990)
		JOC 60 4730 (1995)
Cl	NCS	TL 26 5037 (1985) (chiral) SL 807 (1991)
Br	NBS	TL 26 5037 (1985) (chiral); 36 983 (1995)
I	ICl	JOC 52 4414 (1987)



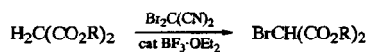
TL 28 5505 (1987)



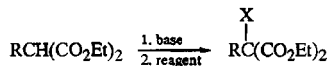
See page 709, Section 1.





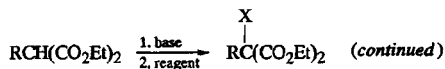
<u>X</u>	
NO ₂	JOC 52 5061 (1987); 54 5453 (1989)
PhSO ₂	JOC 54 5453 (1989)



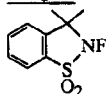
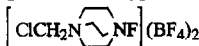
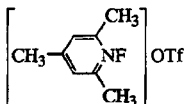
BCSJ 37 547 (1964)



<u>X</u>	<u>Reagent</u>	
F		J Fluorine Chem 52 389 (1991)
	<i>p</i> -TolSO ₂ NFR	JACS 106 452 (1984)
	CF ₃ SO ₂ NF- 	J Fluorine Chem 46 297 (1990)

X

F (continued)

Reagent(PhSO₂)₂NF(CF₃SO₂)₂NFCH₃CO₂FMe₃SiCl / F₂CuCl₂SO₂Cl₂Me₃SiCl, KBrO₃

TL 32 3819 (1991)

SL 187 (1991)

CC 179 (1991)

J Fluorine Chem 58 71 (1992)

TL 27 4465 (1986)

JACS 112 8563 (1990)

JOC 58 2791 (1993)

CC 343 (1994)

JOC 48 724 (1983)

JOC 55 3423 (1990)

JOC 58 4596 (1993)

JOC 29 2706 (1964)

Bull Russ Acad Sci, Div Chem
Sci 41 356 (1992)

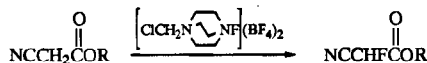
Cl

Br

CuBr₂BrCCl₃

JOC 58 4596 (1993)

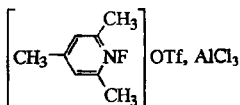
CL 73 (1978)



CC 343 (1994)

XYReagent(s)CO₂R

F



JACS 112 8563 (1990)

Cl

CF₃SO₂Cl, Et₃N or DBU

TL 3643 (1979)

JACS 110 5533 (1988)

JOC 29 2706 (1964)

SO₂Cl₂

CN

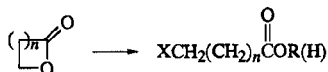
Cl

CF₃SO₂Cl, Et₃N or DBU

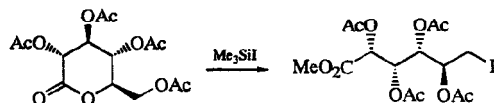
TL 3643 (1979)

JACS 110 5533 (1988)

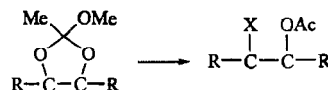
JOC 29 2706 (1964)

SO₂Cl₂

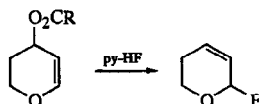
<u>X</u>	<u>Reagent(s)</u>	<u>n</u>	
Cl	MgCl ₂ , <i>n</i> -Bu ₄ NCl	1	JOC 54 2311 (1989)
	SOCl ₂ , MeOH	2	SL 233 (1991)
Br	HBr	1, 2, 4	Coll Czech Chem Commun 32 2485 (1967) Org Prep Proc Int 5 1 (1973) SL 63 (1993) TL 36 7387 (1995)
	HBr, HOAc	3	SL 34 (1990)
	Ph ₃ PBr ₂ /H ₂ O or ROH	2-5	JOC 40 1640 (1975); 53 4978 (1988)
	MgBr ₂	1	JOC 54 2311 (1989)
I	PhNEt ₂ , BI ₃ /H ₂ O or ROH	2-4	TL 32 6855 (1991)
	Me ₃ SiI/ROH	1-4	Syn Commun 11 763 (1981) TL 34 7557 (1993); 35 9337 (1994)
	MgI ₂	1	JOC 54 2311 (1989)



TL 35 5445 (1994)

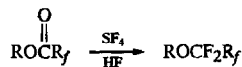


<u>X</u>	<u>Reagent(s)</u>	
Cl	Me ₃ SiCl	Tetr 48 10515 (1992)
Br	AcBr	Tetr 48 10515 (1992)
		JOC 59 5104 (1994)
I	AcCl, NaI	Tetr 48 10515 (1992)

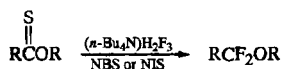


TL 29 1363 (1988)

MgBr₂ SL 243 (1995)Me₃SiBr, cat ZnI₂ TL 33 3443 (1992)



JOC 29 1 (1964)

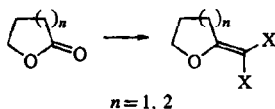


SL 251 (1994)



SL 583 (1991)

JOC 59 5752 (1994)



X

F

Cl

ReagentsCF₂Br₂, P(NMe₂)₃

CC 1437 (1989)

CCl₄, P(NMe₂)₃

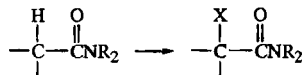
CC 449 (1984)

JCS Perkin I 1471 (1992)

CCl₄, PPh₃

SL 583 (1991)

JOC 59 5752 (1994)

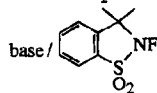
7. Amides

X

F

Reagent(s)base / ArSO₂NFR

JACS 106 452 (1984)



TL 32 1779 (1991) (mono- and difluorination)

Et₃N·3HF, electrolysis

TL 31 3137 (1990)

Br

NBS

JACS 108 1103 (1986); 110 8526 (1988)

Br₂, PBr₃

JACS 80 6238 (1958)

Br₂, Me₃SiI, TMEDA

JOC 58 3384 (1993)

PCl₅/Br₂, cat I₂

JACS 80 6233 (1958)

I

I₂, s-collidine

TL 33 1299 (1992); 34 2165 (1993)

I₂, 2,6-lutidine

JOC 60 7161 (1995) (R = allylic)

I₂, Me₃SiI, TMEDA

JOC 58 3384 (1993)

I₂, Me₃SiCl, NaI, TMEDA
LDA/I₂

TL 35 3239 (1994)
JACS 114 7007 (1992)



X

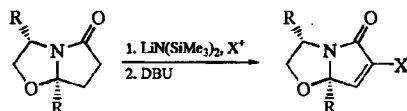
Reagent(s)

Cl

SO₂Cl₂ JOC 37 1526 (1972)
PCl₅ JACS 80 6238 (1958)
PCl₅, POCl₃ JACS 80 6238 (1958)
PCl₅/Cl₂ JACS 80 6233 (1958)
POCl₃/PCl₅/SO₂Cl₂ Helv 41 181 (1958)
ClCOCl/Cl₂ JACS 80 6233 (1958)

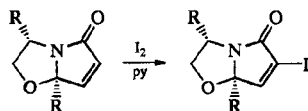
Br

Br₂, PCl₅ TL 32 2469 (1991)
PCl₅/Br₂, cat ZnCl₂ JACS 80 6233 (1958)

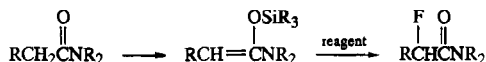


X⁺ = BrCCl₂CCl₂Br, ICH₂CH₂I, NIS

SL 573 (1993)



SL 573 (1993)



Reagent

F₂ JOC 55 3423 (1990)
CF₃OF JACS 102 4845 (1980)
R₂OF JOC 51 1482 (1986)



X

Y

Reagent(s)

RS

F

Et₃N·3HF, electrolysis

TL 33 7017 (1992)

Cl

SO₂Cl₂

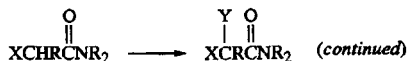
JOC 37 1526 (1972)

RCONH

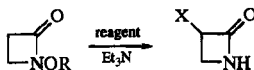
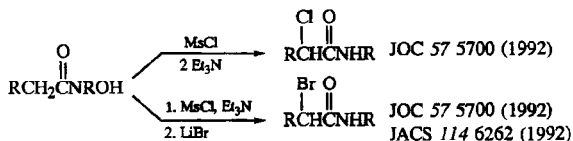
Br

NBS

TL 29 1565 (1988)



<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
CONR ₂	Br	Br ₂ C(CN) ₂ , cat BF ₃ ·OEt ₂	BCSJ 37 547 (1964)
NC	Cl	LDA / NCS	JOC 49 282 (1984)
	Br	Br ₂ C(CN) ₂ , cat BF ₃ ·OEt ₂	BCSJ 37 547 (1964)



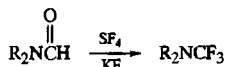
R = Ts, PO(OPh)₂

Reagent = Me₃SiX (X = Cl, Br, I), R₄NX (X = Cl, Br, I)

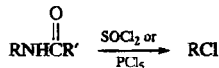
JACS 115 548 (1993)



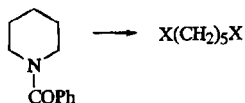
Pol J Chem 56 1369 (1982)



J Fluorine Chem 23 207 (1983)

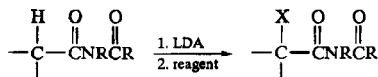


JACS 84 769 (1962)



<u>X</u>	<u>Reagent(s)</u>	
Cl	PCl ₅	JACS 110 5692 (1988)
Br	PBr ₃ , Br ₂	Org Syn Coll Vol 1 428 (1941) JACS 68 2402 (1946); 71 2808 (1949) JOC 51 2206 (1986); 52 5466 (1987)

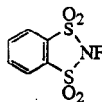
8. Imides and Related Compounds



X

Reagent

F



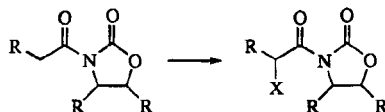
TL 33 1153 (1992)

JOC 60 4730 (1995)

I

I₂

JACS 114 7007 (1992)



X

Reagents

F

NaN(SiMe₃)₂ / (PhSO₂)₂NF

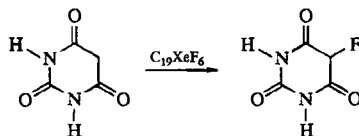
TL 35 3263 (1994)

Br

n-Bu₂BOTf, *i*-Pr₂NEt / NBSTL 28 1123 (1987); 30 6841, 6845 (1989);
35 2301 (1994)

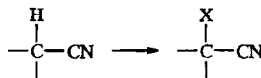
JACS 112 4011 (1990)

JOC 60 2630 (1995)



TL 21 277 (1980)

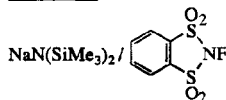
9. Nitriles



X

Reagent(s)

F



JOC 60 4730 (1995)

Cl

PCl₅

JACS 70 165 (1948); 73 103 (1951)

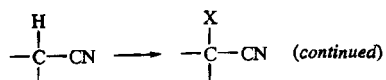
TL 437 (1967)

Org Syn 58 67 (1978)

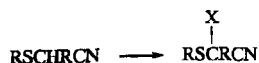
Org Syn Coll Vol 6 427 (1988)

JOC 48 1000 (1983)

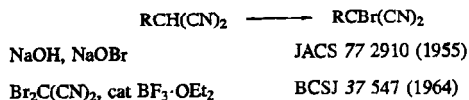
PCl₅, py



<u>X</u>	<u>Reagent(s)</u>	
Br	Br ₂	Bull Soc Chim Belg 43 200 (1934) Arkiv Kemi 12A 22 (1937) JACS 71 2254 (1949) Org Syn Coll Vol 3 347 (1955) Carbohydr Res 124 43 (1984)
	Br ₂ , PBr ₃	JACS 70 165 (1948); 73 103 (1951)
	NBS	Carbohydr Res 124 43 (1984)



<u>X</u>	<u>Reagent</u>	
Cl	SO ₂ Cl ₂	TL 28 2591 (1987)
Br	Br ₂	TL 3813 (1977)



12. HALODECARBOXYLATION AND DECARBONYLATION OF ACIDS AND DERIVATIVES



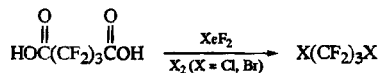
Reviews:

Chem Rev 56 219 (1956) (Hunsdiecker reaction)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 5.4, p 717

<u>X</u>	<u>Reagent(s)</u>	
F	XeF ₂ , (HF)	JOC 48 4158 (1983); 58 705 (1993) Can J Chem 64 138 (1986)
Cl	NCS / Pb(OAc) ₄	Syn 493 (1973) JACS 107 516 (1985)
	Pb(OAc) ₄ , LiCl	JACS 87 2500 (1965); 107 199, 7978 (1985); 113 1386 (1991) JOC 30 3265 (1965) Org Rxs 19 279 (1972) (review) Ann 735 47 (1970)
	Pb(O ₂ CR) ₄ , CCl ₄ , hv	
Br	AgO or KOH-AgNO ₃ / Br ₂	Org Syn Coll Vol 3 578 (1955) Org Rxs 9 332 (1957) JOC 57 5959 (1992)
	Tl ₂ CO ₃ / Br ₂	JCS Perkin I 2608 (1981)
	TlOEt / Br ₂	JOC 34 1172 (1969) JCS Perkin I 2608 (1981)
	HgO, Br ₂ , (hv)	JOC 26 280 (1961); 30 415 (1965); 34 3216 (1969); 37 664 (1972); 44 3405 (1979); 52 460 (1987); 58 3188, 6126 (1993) Org Syn 43 9 (1963) JACS 106 2194 (1984); 109 7230 (1987) Syn Commun 14 983 (1984) (<i>gem</i> - dibromocycloalkanes) TL 27 5371 (1986); 28 5263 (1987) Org Syn Coll Vol 6 179 (1988) TL 36 1233 (1995)
	(COBr) ₂ , hv, (cat Fe)	

<u>X</u>	<u>Reagent(s)</u>	
I	I ₂ (on AgO ₂ CR)	JCS 368 (1941)
	<i>t</i> -C ₄ H ₉ OI, (hν)	JCS 2438 (1965)
		JOC 45 4226 (1980)
	PhI(OAc) ₂ , I ₂ , (hν)	JOC 51 402 (1986)
		CC 675 (1987)
		TL 28 6381 (1987)
	Pb(OAc) ₄ , I ₂	JCS 2438 (1965)
		JOC 31 1857 (1966)
		Org Rxs 19 279 (1972) (review)
	Pb(OAc) ₄ , I ₂ , hν	JOC 58 7876 (1993)
	HgO, I ₂	JOC 37 664 (1972)



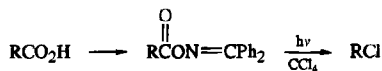
JOC 58 6922 (1993)



<u>X</u>	<u>Reagent</u>	
Cl	NCS	JOC 21 920 (1956)
Br	NBS	JOC 21 920 (1956)
		Org Syn Coll Vol 4 254 (1963)

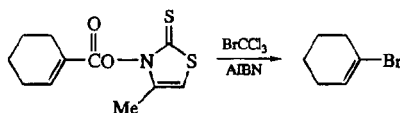


Br ₂ / base	JCS 2012 (1950)
	JACS 75 2645 (1953); 79 5475 (1957); 111 1429 (1989)
	JOC 27 2339 (1962); 30 2208 (1965); 36 1031 (1971); 56 4066, 4341 (1991)
	BSCF 1736 (1971)
	J Chem Res (S) 270 (1981)
	TL 24 2965 (1983); 31 4449 (1990)
	Org Syn 62 39 (1984)
Br ₂ / NaN ₃	Chem Ind 1321 (1970)
	Org Syn Coll Vol 7 172 (1990)
NBS, PhIO or PhI(OAc) ₂	JOC 59 3543 (1994)

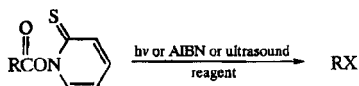


R = 1°, 2°, 3° alkyl; aryl

TL 29 6287 (1988)



JOC 56 6199 (1991)

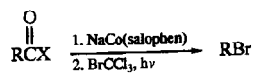


<u>X</u>	<u>Reagent</u>	
Cl	CCl ₄	TL 24 4979 (1983); 29 1449 (1988); 30 2461 (1989) Tetr 41 3901 (1985) JOC 54 6101 (1989)
	Cl ₃ CF	JOC 59 2986 (1994)
	Cl ₃ CCF ₃	JOC 60 5303 (1995)
Br	BrCCl ₃	TL 24 4979 (1983); 26 5939 (1985); 30 2461 (1989); 34 3335 (1993); 35 2787 (1994); 36 6471 (1995) Tetr 41 3901 (1985); 43 4321 (1987) JOC 54 6101 (1989); 55 1169 (1990); 57 3483 (1993); 59 7625 (1994)
	BrCHClCF ₃	JOC 59 2986 (1994); 60 5303 (1995)
I	HCl ₃	TL 24 4979 (1983); 30 2461 (1989) Tetr 41 3901 (1985); 43 4321 (1987) JOC 54 6101 (1989)
	H ₂ Cl ₂	Tetr 43 4321 (1987)
	CF ₃ CH ₂ I	JACS 110 7230 (1988)
		TL 30 6967 (1989) JOC 57 5959 (1992); 58 7876 (1993); 60 5303 (1995)



Review: Syn 157 (1969)

<u>X</u>	<u>R</u>	<u>Catalyst</u>	
Cl	alkyl, aryl	ClRh(PPh ₃) ₃	JACS 88 3452 (1966); 89 2338 (1967); 90 99 (1968)
	aryl	Pd-C, PdCl ₂ or Pd(PPh ₃) ₄	TL 23 371 (1982)
Br	aryl	ClRh(PPh ₃) ₃	JACS 89 2338 (1967)
		ClRh(CO)(PPh ₃) ₂	JACS 90 99 (1968)
I	aryl	ClRh(PPh ₃) ₃	JOC 33 1928 (1968)



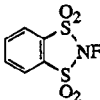
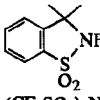

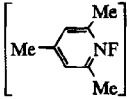
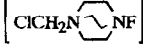

R = aryl, vinylic; X = Cl, O₂CR

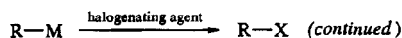
TL 29 707 (1988)



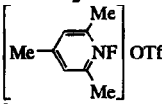

13. HALOGENATION OF ORGANOMETALLICS

Review: Tetr 45 6601 (1989) (radiolabeled compounds)

See also page 410, Section 2, for additional preparations of vinylic halides via hydrometallation halogenation.

			$R-M \xrightarrow{\text{halogenating agent}} R-X$	
<u>M</u>	<u>R</u>	<u>X</u>	<u>Reagent(s)</u>	
Li	aryl	F	$(PhSO_2)_2NF$	SL 187 (1991) TL 35 3465 (1994)
				TL 35 3465 (1994) JOC 60 4730 (1995)
				TL 32 3819 (1991)
	alkynyl	I	$(CF_3SO_2)_2NF$ ICH_2CH_2I	JOC 60 4730 (1995) TL 35 3673 (1994) See page 669, Section 4.
MgX	alkyl	F		JOC 55 3373 (1990)
			 OTf	TL 27 4465 (1986)
			 $(BF_4)_2$	JOC 58 2791 (1993)
	aryl	F	 $(n = 1, 2)$	JOC 55 3373 (1990)



<u>M</u>	<u>R</u>	<u>X</u>	<u>Reagent(s)</u>	
MgX (cont'd)	aryl	F		J Fluorine Chem 52 389 (1991)
			<i>p</i> -TolSO ₂ NF- <i>t</i> -Bu	JACS 106 452 (1984)
				TL 32 1631 (1991) JOC 60 4730 (1995)
			 OTf	TL 27 4465 (1986)
			 (BF ₄) ₂	JOC 58 2791 (1993)
B(OH) ₂	aryl	F	CsSO ₄ F (HOCH ₂ CH ₂) ₂ NMe, CsSO ₄ F	Tetr 48 8073 (1992) SL 761 (1990) Tetr 48 8073 (1992)
			Br ₂	JACS 74 5068 (1952); 77 4834 (1955)
		I	NaBr, <i>p</i> -TsN(Cl)Na·3H ₂ O I ₂	Org Prep Proc Int 14 359 (1982) JACS 76 2679 (1954)
			NaI, <i>p</i> -TsN(Cl)Na·3H ₂ O	Austral J Chem 18 1527 (1965) Org Prep Proc Int 14 359 (1982)
	reviews	—	—	Syn 761 (1979) E. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981) W. P. Weber, "Silicon Reagents for Organic Synthesis," Springer Verlag, New York (1983)
SiR ₃	aryl	F	F ₂ CH ₃ CO ₂ F XeF ₂	J Fluorine Chem 30 97 (1985) J Fluorine Chem 30 97 (1985) SL 753 (1993)
			Cl ₂	JCS 179 (1960) JOC 28 3272 (1963)
		Br	Br ₂	JCS 433 (1948); 4449 (1957); 3031, 3034 (1959); 179 (1960) JCS Perkin I 2481 (1972)
			NaBr, NCS	J Label Cpd Radiopharm 19 1171 (1982) JOC 48 1542 (1983)
			Br ⁻ , <i>t</i> -BuOCl	J Label Cpd Radiopharm 19 1171 (1982)
			NBS	J Label Cpd Radiopharm 19 1171 (1982)


			NBS, Cl^-	J Label Cpds Radiopharm 19 1171 (1982)
	I		I_2	JCS 433 (1948)
			ICl	JOC 28 3272 (1963)
				JCS Perkin I 2481 (1972)
				J Label Cpds Radiopharm 19 1171 (1982)
			NaI , NCS	J Label Cpds Radiopharm 19 1171 (1982)
				JOC 48 1542 (1983)
			NaI , $t\text{-BuOCl}$	J Label Cpds Radiopharm 19 1171 (1982)
	alkynyl	Br	NBS, cat AgNO_3	SL 485 (1994)
		I	ICl	JOMC 37 41 (1972)
			NIS, cat AgNO_3	SL 485 (1994)
SnR_3	aryl	F	F_2	CC 733 (1981)
				Can J Chem 61 658 (1983)
				J Fluorine Chem 25 329 (1984)
				BSCF 930 (1986)
				Appl Radiat Isot 43 989 (1992); 44 527 (1993)
				JOC 60 227 (1995)
			OF_2	Appl Radiat Isot 43 989 (1992)
			CF_3OF	BSCF 930 (1986)
			$\text{CH}_3\text{CO}_2\text{F}$	J Fluorine Chem 25 329 (1984)
				Appl Radiat Isot 43 989 (1992); 44 527 (1993)
				J Label Cpds Radiopharm 34 565 (1994)
			CsSO_4F	CC 1623 (1986)
				BSCF 930 (1986)
		Br	Br_2	CC 840 (1972)
				JCS Perkin I 2481 (1972)
		I	I_2	JCS 681 (1963)
				Bull Soc Chim Belg 72 286 (1963); 77 15 (1968)
				Helv 47 1679, 1688, 2037 (1964)
			ICl	CC 840 (1972)
				JCS Perkin I 2481 (1972)
			NaI , $\text{CH}_3\text{CO}_2\text{H}$	JACS 117 3084 (1995)
SeR	alkyl	Br	Br_2 , Et_3N	TL 2647 (1976)
HgX	reviews	—	—	F. R. Jensen, "Electrophilic Substitution of Organomercurials," McGraw Hill, New York (1968)
				Tetr 38 1713 (1982)
				R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer, New York (1985), Chpt 3
	alkyl	F	F_2	Bull Acad Sci USSR, Div Chem Sci 1280 (1968); 1483 (1969)

$R-M \xrightarrow{\text{halogenating agent}} R-X$ (continued)			
<u>M</u>	<u>R</u>	<u>X</u>	<u>Reagent(s)</u>
HgX (cont'd)	alkyl	Cl	Cl ₂
			Helv 48 366 (1965) JACS 90 5793 (1968) Bull Acad Sci, Div Chem Sci 641 (1969) JOC 41 1529 (1976) JACS 81 1261, 1262 (1959); 82 148, 2466 (1960); 84 2203 (1962); 90 5793 (1968) JCS Perkin I 695 (1975) JOC 41 1529 (1976); 43 4048 (1978); 44 3461 (1979) JCS 823 (1933); 535 (1935) JACS 61 1585 (1939); 78 2597 (1956) JOC 28 184 (1963); 35 3390 (1970) Helv 54 578, 2628 (1971); 55 2731 (1972) BSCF 930 (1986) J Gen Chem USSR 40 2768 (1970) JOMC 61 33 (1973) CC 217 (1981) Ber 35 2853 (1902) JCS 637, 3215 (1926) Org Syn 7 12 (1927) Can J Chem 39 1827 (1961) Bull Acad Sci USSR, Div Chem Sci 218 (1965) JOC USSR 4 1077 (1968) JOMC 61 33 (1973) CC 217 (1981) Ber 31 2154 (1898); 101 2004 (1968); 107 1195 (1974) JCS 637 (1926) Org Syn Coll Vol I 325, 326 (1941) JOC USSR 4 905, 1077, 1080 (1968) JOMC 61 33 (1973) Austral J Chem 26 541 (1973); 28 1499 (1975) CC 217 (1981)
		Br	Br ₂
		I	I ₂
	aryl	F	CF ₃ OF
		Cl	Cl ₂
		Br	NCS Br ₂
		I	I ₂

$RCH=CHM \longrightarrow RCH=CHX$			
<u>M</u>	<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry</u>
Li	F	(PhSO ₂) ₂ NF	retention
BX ₂	—	—	—

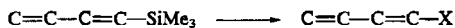
SL 187 (1991)

See also page 421, Section 2.8.

BBr ₂	Br	Br ₂ /NaOH	inversion	JOC 54 6068 (1989)
	I	I ₂ /NaOH	retention	JOC 54 6068 (1989)
		NaOH/I ₂	retention	JOC 45 389 (1980)
	Br	Br ₂ /NaOMe	inversion	JACS 95 6456 (1973) Syn 480 (1986) TL 29 21 (1988) JOC 54 6068 (1989)
	I	ICl, NaOAc	retention	Syn Commun 11 247 (1981)
		ICl/NaOMe	inversion	TL 36 3929 (1995)
		NaOMe/ICl	retention	TL 36 3929 (1995)
		py/I ₂	retention, inversion	JOC 54 6068 (1989)
B(OH) ₂	Cl	Cl ₂ /Na ₂ SO ₃	inversion	TL 26 279 (1985)
	I	NaOH/I ₂	retention	JACS 95 5786 (1973) JOC 45 389 (1980) CC 446 (1990)
		NaOAc/I ₂	retention	Syn Commun 11 247 (1981)
BR ₂	Cl	Cu ₂ Cl ₂ , H ₂ O, HMPA	retention	JCS Perkin I 2725 (1992)
	Br	Cu ₂ Br ₂ , Cu(OAc) ₂ , H ₂ O, HMPA	retention	JCS Perkin I 2725 (1992)
		Br ₂ /Δ	retention	JACS 89 4531 (1967) JOC 54 6068 (1989)
		Br ₂ /H ₂ O	inversion	JACS 89 4531 (1967) JOC 54 6068 (1989)
SiX ₃	reviews	—	—	Syn 761 (1979) Org Rxs 37 57 (1989) See also page 432, Section 2.10.
SiR ₃	Cl	Cl ₂ /KOH	?	JACS 76 1613 (1954)
		Cl ₂ /NaOMe	inversion	TL 543 (1974) Syn Commun 7 475 (1977) JOC 43 4424 (1978)
		Cl ₂ /alumina	inversion	Syn Commun 7 475 (1977) JOC 43 4424 (1978)
		Cl ₂ /KF·2H ₂ O	inversion	JOC 43 4424 (1978)
		ICl/KF·2H ₂ O	inversion	Syn Commun 8 291 (1978)
		LiCl, XeF ₂	?	TL 31 5633 (1990)
		m-ClC ₆ H ₄ CO ₂ H/ HCl/BF ₃ ·OEt ₂	inversion	JOC 54 868 (1989)
	Br	Br ₂	retention	TL 2533 (1973) JOMC 121 293 (1976)
		Br ₂	inversion	TL 3317 (1977)
		Br ₂ /KOH	?	JACS 76 1613 (1954)
		Br ₂ /NaOMe	inversion	TL 543 (1974) Syn Commun 7 475 (1977) JOC 43 4424 (1978)
		Br ₂ /NaOMe	retention	JOC 44 4623 (1979); 54 868 (1989)

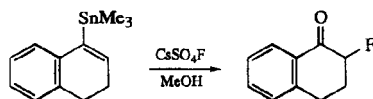
		$RCH=CHM \longrightarrow RCH=CHX$ (continued)	
<u>M</u>	<u>X</u>	<u>Reagent(s)</u>	<u>Stereochemistry</u>
SiR ₃ (cont'd)	Br	Br ₂ /alumina	inversion Syn Commun 7 475 (1977) JOC 43 4424 (1978); 52 1100 (1987); 59 2020 (1994)
		Br ₂ /KF·2H ₂ O	inversion JOC 43 4424 (1978)
		Br ₂ / <i>n</i> -Bu ₄ NF	inversion TL 28 2033 (1987) JOC 55 5324 (1990); 58 5452 (1993)
		(C ₅ H ₅ NH)Br ₃	inversion TL 34 3177 (1993)
		BrCN, AlCl ₃	retention TL 3317 (1977)
		NBS	mixture JOC 52 1100 (1987)
		LiBr, XeF ₂	? TL 31 5633 (1990)
		<i>m</i> -ClC ₆ H ₄ CO ₃ H/ HBr/BF ₃ ·OEt ₂	inversion JACS 99 1993 (1977) JOC 54 868 (1989)
		I ₂	retention TL 543 (1974); 3317 (1977)
		I ₂ , AgO ₂ CCF ₃ / KF·2H ₂ O	inversion TL 543 (1974)
	I	I ₂ , AlCl ₃ or SnCl ₄	mixture TL 27 883 (1986)
		ICl	retention JOC 54 868 (1989)
		ICl/alumina	inversion JOC 52 1100 (1987)
		ICl/KF	inversion Syn Commun 8 291 (1978) JOMC 285 109 (1985)
		ICl/KF	retention Syn Commun 8 291 (1978)
		I(py) ₂ BF ₄ , HBF ₄	retention TL 36 2153 (1995)
		LiI, XeF ₂	? TL 31 5633 (1990)
		<i>m</i> -ClC ₆ H ₄ CO ₃ H/HI/ LiBF ₄	inversion JOC 59 332 (1994)
		<i>m</i> -ClC ₆ H ₄ CO ₃ H/HF/ BF ₃ ·OEt ₂	inversion JOC 54 868 (1989)
SiF ₃	Br	Br ₂	inversion JOC 52 1100 (1987)
		NBS	mixture JOC 52 1100 (1987)
	I	ICl/alumina	inversion or retention JOC 52 1100 (1987)
	Cl	Cl ₂	retention Organomet 1 355 (1982)
		CuCl ₂	retention Organomet 1 369 (1982)
SiF ₃ ²⁻	Br	Br ₂	retention Organomet 1 355 (1982)
		NBS	retention Organomet 1 355 (1982)
	CuBr ₂		retention Organomet 1 369 (1982)
		I ₂	retention Organomet 1 355 (1982)
	I		
SnR ₃	F	$\left[\text{ClCH}_2\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \text{NF} \right] (\text{BF}_4)_2$? TL 34 3057 (1993)
		CsSO ₄ F	? SL 831 (1992)
		XeF ₂ , AgPF ₆	retention Syn Commun 22 1461 (1992)
		XeF ₂ , AgOTf	retention SL 207 (1993)
	Cl	Cl ₂	? Syn Commun 24 755 (1994)
		MeLi/MgBr ₂ / PhSO ₂ Cl	? JOC 49 3438 (1984)
			JACS 115 6625 (1993)
		CuCl ₂	retention TL 32 6563 (1991)

HgX	Br	Br ₂	retention	JOC 43 3450 (1978); 51 277 (1986); 52 3687 (1987) JACS 106 5734 (1984); 107 7515 (1985) TL 29 2783 (1988) Syn Commun 24 755 (1994)
		NBS	?	TL 32 6563 (1991)
		CuBr ₂	?	TL 32 6563 (1991)
	I	I ₂	retention	JOC 43 3450 (1978); 52 3687 (1987); 55 5324 (1990); 59 2695, 4143 (1994); 60 764 (1995) JCS Perkin I 1317 (1981) TL 23 3851 (1982); 28 2033 (1987); 30 3613 (1989); 32 3329 (1991); 34 6407 (1993) JACS 109 2138 (1987); 114 10653 (1992); 115 1619, 11393 (1993) SL 998 (1994) Syn Commun 24 755 (1994)
		NIS	retention	TL 36 3605 (1995)
		NaI, chloramine-T	retention	TL 30 3613 (1989)
	Cl	Cl ₂	?	Ber 42 4232 (1909)
	Br	Br ₂ , py	retention	JOC 38 3406 (1973)
		Br ₂ , CS ₂	inversion	JOC 38 3406 (1973)
	I	I ₂ , polar solvent	retention	Bull Acad Sci USSR, Div Chem Sci 1985 (1961); 1093 (1966) Proc Acad Sci USSR, Chem Sec 161 286 (1965)



X = Br, I; reagents = Br₂, NBS, I₂, NIS

JOC 59 5527 (1994)



SL 831 (1992)

AMINES

GENERAL REFERENCES

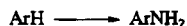
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- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E16c (aziridines and azetidines), G. Thieme, Stuttgart-New York (1992)
- Contemporary Organic Synthesis 1 475 (1994)

1. FROM ALKANES



Tetr 23 3563 (1967)

2. FROM ARENES



HN_3 , H_2SO_4 or AlCl_3

Ber 57 704 (1924)
JCS 4685 (1961)
JACS 86 1588 (1964)

HN_3 , AlCl_3

JACS 86 1588 (1964)

Me_3SiN_3 , $\text{CF}_3\text{SO}_3\text{H}$

JOC 54 1203 (1989)

$\text{N} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{NNH}_2$, $\text{KO}-i\text{-Bu}$ (ArNO_2)

JOC 51 5039 (1986); 53 3978 (1988)

$(\text{PhN}_2)\text{Cl}/\text{Na}_2\text{S}_2\text{O}_4$

JACS 106 2651 (1984)

RSNH_2 , $\text{KO}-i\text{-Bu}$ (ArNO_2)

JOC 57 4784 (1992)

$\text{Cl}_3\text{CCH}_2\text{O}_2\text{CN}=\text{NCO}_2\text{CH}_2\text{CCl}_3$, $\text{CF}_3\text{SO}_3\text{H}$ or
 $\text{CF}_3\text{CO}_2\text{H}/\text{Zn}$, HOAc

JOC 60 4268 (1995)

$\text{Cl}_3\text{CCH}_2\text{O}_2\text{CN}=\text{NCO}_2\text{CH}_2\text{CCl}_3$, LiClO_4/Zn ,
 HOAc

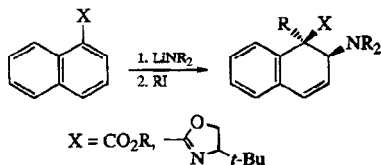
TL 34 2441 (1993)

$\text{Cl}_3\text{CCH}_2\text{O}_2\text{CN}=\text{NCO}_2\text{CH}_2\text{CCl}_3$, $\text{BF}_3\cdot\text{OEt}_2$ or
 ZnI_2/Zn , HOAc

JOC 59 682 (1994); 60 4268 (1995)

$\text{Cl}_3\text{CCH}_2\text{O}_2\text{CN}=\text{NCO}_2\text{CH}_2\text{CCl}_3$, ZnCl_2/Zn ,
 HOAc

JOC 59 682 (1994); 60 4268 (1995)



JOC 60 7445 (1995)

3. FROM ALKENES, DIENES AND ALKYNES

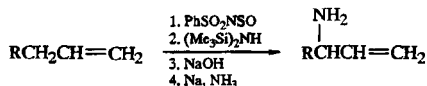
Reviews:

Tetr 39 703 (1983)

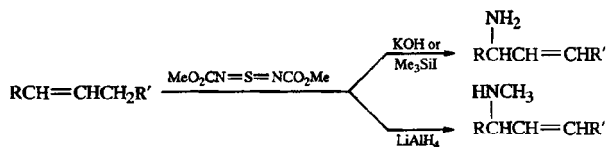
J Moi Catal 49 235 (1989)

For analogous syntheses of amides and sulfonamides, see also page 1628, Section 3.

For alkyne \rightarrow enamine, see also page 418, Section 2.4.

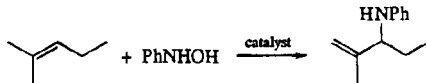


Tetr 44 4243 (1988)



JOC 48 3561 (1983); 59 8297 (1994)

Org Syn Coll Vol 8 427 (1993)



Catalyst

$\text{MoO}_2\text{L}_2(\text{HMPA})$

CC 853 (1992)

JOC 59 5365 (1994)

$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$

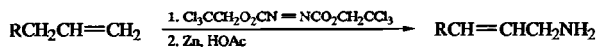
TL 35 8739 (1994)

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

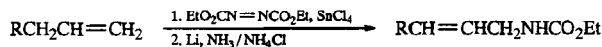
TL 35 8739 (1994)

Fe phthalocyanine

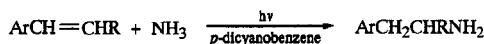
JOC 59 214 (1994); 60 5979 (1995)



JOC 56 1971 (1991)

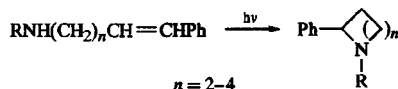


JOC 58 5261 (1993)



JOC 57 1351 (1992)

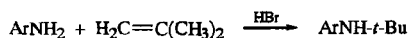
TL 34 5131 (1993)



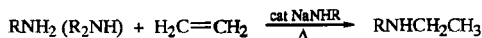
JACS 111 6465 (1989)

TL 31 5293 (1990); 33 4249 (1992)

JOC 58 6390 (1993)

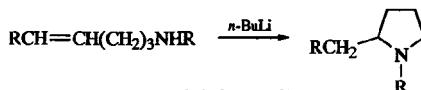


JOC 60 2613 (1995)

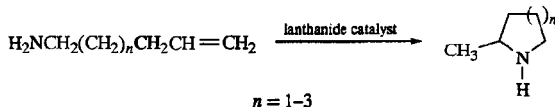


JOC 22 646 (1957)

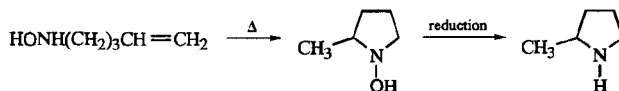
Org Syn Coll Vol 5 575 (1973)



TL 33 6359 (1992)



JACS 111 4108 (1989); 114 275 (1992); 116 10241 (1994) (chiral)

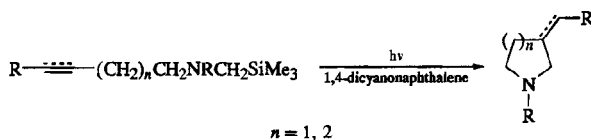


JOC 41 855, 863 (1976); 53 1768 (1988); 55 3007 (1990); 60 5803 (1995)

Austral J Chem 31 2317 (1978)

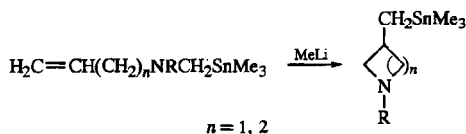
CC 169 (1993)

JACS 116 3139 (1994)



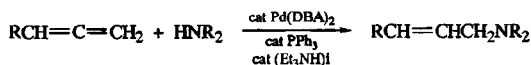
TL 30 6059 (1989); 33 6533 (1992); 35 8319 (1994)

Tetr 50 8185 (1994)

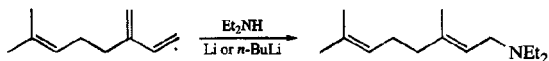


JCS Perkin I 1275 (1993)

TL 36 2157 (1995)

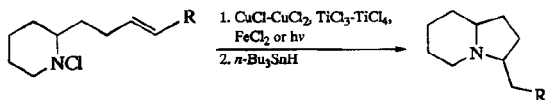


TL 36 3857 (1995)



BCSJ 46 222 (1973)

Org Syn Coll Vol 8 222 (1993)



BSCF 111, 115 (1970)

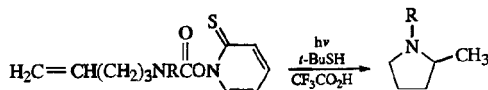
TL 3107 (1970); 903 (1971); 2191 (1974); 22 61 (1981)

Acct Chem Res 8 165 (1975)

Tetr 37 2843 (1981)

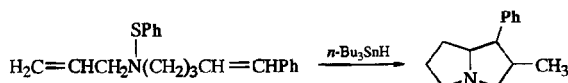
Angew Int 22 337 (1983) (review)

JOC 51 5043 (1986); 53 2144 (1988)

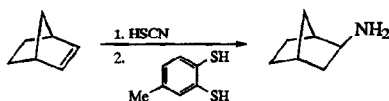


JACS 109 3163 (1987)

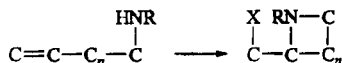
TL 31 1675 (1990)



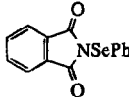
TL 33 4993 (1992)

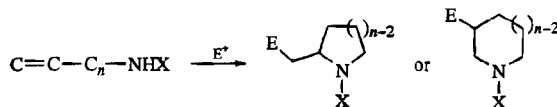


TL 33 3599 (1992)

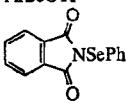


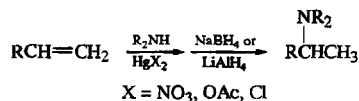
Review: P. A. Bartlett, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Part B, Chpt 6

<u>X</u>	<u>Reagent(s)</u>	
Br	Br ₂	JOC 44 330 (1979)
I	I ₂ , (NaHCO ₃)	JOC 54 3374 (1989); 60 7357 (1995)
	I ₂ , KI	TL 30 1327 (1989) (R = OR) Proc Acad Sci USSR, Chem Sec 146 787 (1962)
PhSe	PhSeX (X = Cl, Br)	JOC 44 287 (1979)
		TL 35 5065 (1994) JACS 107 3891 (1985)
HgX	HgX ₂	JOC 44 330 (1979) TL 26 1123, 4981 (1985); 32 3205 (1991) R. C. Larock, "Solvomercuration / Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 6 (review)



<u>X</u>	<u>E⁺</u>	<u>n</u>	<u>Ring size</u>	
COR	I ₂	3	5	TL 4993 (1979)
	PhSBr	3	5	TL 4993 (1979)
	Hg(OAc) ₂	3	5	TL 4993 (1979); 24 15, 2051 (1983)
				JOC 44 330 (1979); 46 3920 (1981)
CO ₂ R	I ₂ , NaHCO ₃	3	5, 6	TL 25 1065 (1984)
				JOC 53 5491 (1988)
	PhSeCl, silica gel	3	5	JOC 45 2120 (1980)
		4	6	JOC 45 2120 (1980)

ArSeOTf	3	6	JOC 60 4660 (1995)
	3	5	JACS 101 3704 (1979) TL 24 1357 (1983) Tetr 41 4835 (1985) TL 24 1357 (1983)
(PhTeO)O ₂ CCF ₃	4	6	JOC 54 4398 (1989)
	3	5	JOC 54 4398 (1989)
	4	6	JOC 54 4398 (1989)
Hg(OAc) ₂	3	5	JOC 46 3920 (1981); 49 40, 2838 (1984); 57 4401 (1992) TL 24 11 (1983)
Hg(O ₂ CCF ₃) ₂	3	5	JOC 49 2838 (1984)
	4	6	JOC 49 2838 (1984); 60 6941 (1995)
SO ₂ Ar			
NBS	3	5	TL 25 1065 (1984)
	3	5, 6	JOC 53 5491 (1988)
	4	6	JOC 53 5491 (1988)
I ₂ , NaHCO ₃	3	5	TL 25 1065 (1984)
	3	5, 6	JOC 53 5491 (1988)
NIS	3	5	TL 25 1065 (1984) JOC 53 5491 (1988)



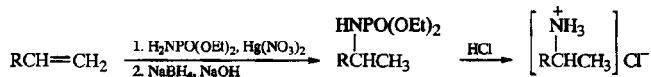
Compt Rend C 262 1591 (1966); 272 1141 (1971)

TL 5165 (1967); 2289 (1969); 4399 (1971)

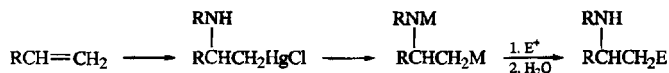
BSCF 583 (1970)

Syn 806 (1974); 116, 467 (1975)

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 6 (review)



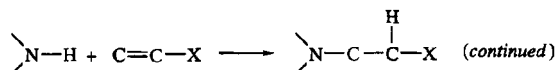
Syn 918 (1982)



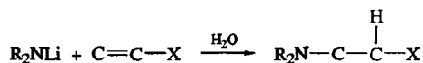
M = alkali metal; E⁺ = D₂O, O₂, CO₂, RCHO, R₂CO, Me₃SiCl, RX, (MeS)₂, R₂C=NR

TL 2015 (1978)

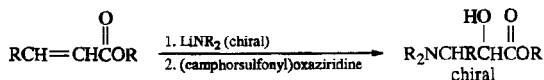
JOC 44 4798 (1979); 46 1281 (1981); 47 1560 (1982)



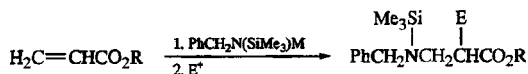
<u>X</u>	<u>Amine</u>	<u>Reagents</u>	
CO ₂ R (<i>cont'd</i>)	R ₂ NH (<i>cont'd</i>)	cat FeCl ₃ cat Yb(OTf) ₃ , high pressure	TL 30 3969 (1989) TL 36 233 (1995)
CO ₂ R (lactone)	RNH ₂	—	TL 29 1303 (1988); 36 7133 (1995)
	R ₂ NH	guanidinium salt	TL 36 3941 (1995)
CONHR	NH ₃ , RNH ₂	—	TL 36 7371 (1995)
	R ₂ NH	—	BSCF 1717 (1971) TL 36 7371 (1995)
CONR (lactam)	RNH ₂ , R ₂ NH	—	JOC 60 3189 (1995)
CONROR	RNH ₂ , R ₂ NH	—	TL 35 5157 (1994)
CN	NH ₃ , RNH ₂ , R ₂ NH	review	Org Rxs 5 79 (1979)
	NH ₃	—	Org Syn Coll Vol 3 93 (1955)
	RNH ₂	—	JCS 399 (1945) BSCF 1717 (1971) Chem Pharm Bull 25 1319 (1977) Syn 732 (1981) TL 28 1757 (1987) (intramolecular) JACS 112 6696 (1990) JOC 58 6596 (1993) JOC 54 220 (1989) Org Syn Coll Vol 4 146 (1963) BSCF 1717 (1971) JOC 58 3736 (1993); 60 7238 (1995)
SOAr	RNH ₂	—	TL 29 2089 (1988)

X

CO ₂ R	JOC 57 2114 (1992); 59 649 (1994); 60 143 (1995) (all chiral) CC 1660 (1993) (chiral) SL 461 (1993); 117 (1994) (both chiral) TL 36 8391 (1995)
CON(OMe)Me	SL 700 (1995) (chiral)



SL 731 (1993)

E⁺ = H⁺, RX, RCHO, internal RCH=CHCO₂R, Me₃SiCl (on oxygen)M

Li

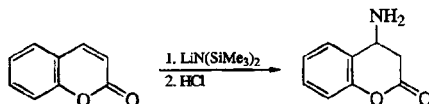
CC 1410 (1987); 753 (1989)
 Tetr 44 4173 (1988); 46 4563 (1990)
 JOC 57 3139 (1992); 58 7948 (1993)
 JACS 115 10139 (1993)
 TL 35 8425 (1994)

Cu

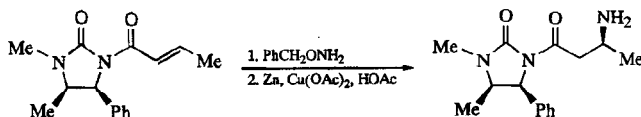
JACS 114 5427 (1992)
 JOC 57 5049 (1992); 59 4068 (1994)

Zn

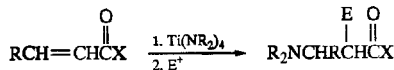
JOC 57 5049 (1992)



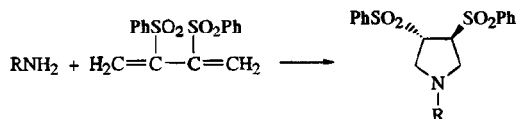
TL 35 6599 (1994)



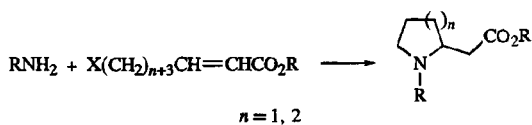
JOC 58 5615 (1993)

X = R, OR; E⁺ = RCHO-BF₃·OEt₂, RCH(OMe)₂-SnCl₄

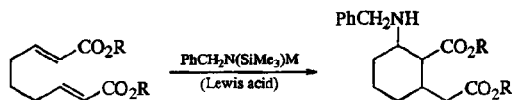
TL 32 2371 (1991)



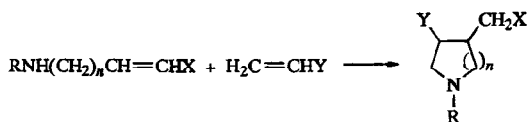
TL 29 3041 (1988)



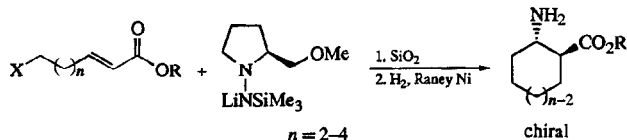
JOC 57 1727 (1992)

 $\text{M} = \text{Li, Cu, Zn}$

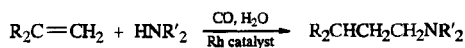
JOC 57 5049 (1991)

 $n = 1, 2; \text{X} = \text{COR, CO}_2\text{R}; \text{Y} = \text{NO}_2, \text{COR}$

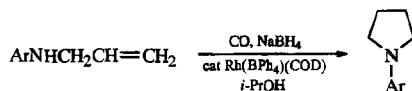
TL 31 3039, 4917 (1990)



SL 369 (1995)



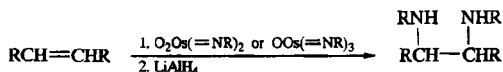
JOC 47 445 (1982); 60 6612 (1995)



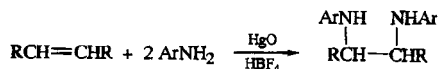
JOC 57 3328 (1992)



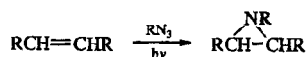
JACS 107 2931 (1985)



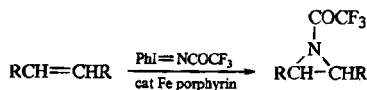
JACS 99 3420 (1977)



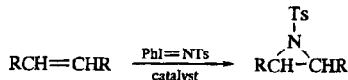
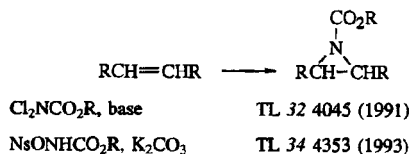
JOC 56 2930 (1991)



See page 815, Section 6.



CC 1161 (1984)

Catalyst

Mn porphyrin	CC 1161 (1984) JOC 56 6744 (1991)
Mn salen	TL 33 1001 (1992) SL 469 (1993) (chiral)
Fe porphyrin	CC 1161 (1984) JCS Perkin II 1517 (1988) JOC 56 6744 (1991)
Cu(acac) ₂	JOC 56 6744 (1991) JACS 116 2742 (1994) SL 949 (1995) (1,3-dienes)
CuClO ₄	JOC 56 6744 (1991) JACS 116 2742 (1994)
Cu(OTf) ₂	JACS 116 2742 (1994)
CuPF ₆ , bis(imine) (chiral)	JACS 117 5889 (1995)
CuOTf, bis(imine) (chiral)	JACS 115 5326 (1993)
CuOTf, bis(oxazoline) (chiral)	JACS 113 726 (1991); 115 5328 (1993)

CuOTf or Cu(OTf)₂, bis(aziridine) (chiral)

TL 35 4631 (1994)

Cu(C₂H₄)[hydrotris(3,5-dimethyl-1-pyrazolyl)-borate]

Organomet 12 261 (1993)

XY

OR

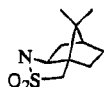
Cl

JOC 56 3323 (1991)

NR₂

I

TL 36 3491 (1995)



Br

TL 35 1653 (1994)

(M = Na, *n*-Bu₄N)

TL 29 4309 (1988)

X = Ar, CO₂R, CONR₂CF₃CO₂H

Chem Pharm Bull 33 2762 (1985)

TL 32 1245 (1991); 33 3575, 6607 (1993); 34 3279, 8187 (1993)

JOC 60 3787 (1995)

LiF, ultrasound

JOC 52 235 (1987)

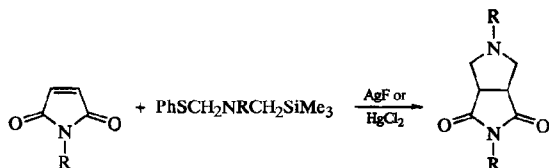
Org Syn Coll Vol 8 231 (1993)

CsF, Me₃SiF or Me₃SiOTf

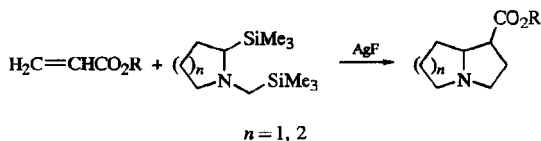
CL 1117 (1984)



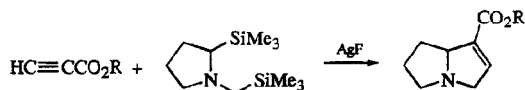
Chem Pharm Bull 33 2762 (1985)



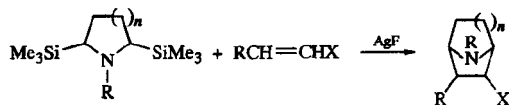
Ber 119 813 (1986)



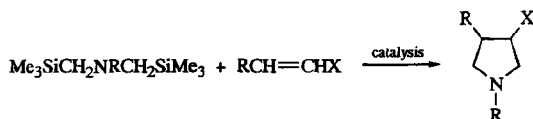
TL 34 4861 (1993)



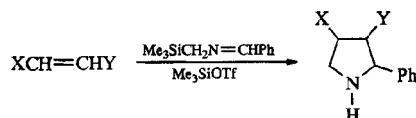
SL 277 (1994)

 $n = 1-3$; $\text{X} = \text{CHO}, \text{CO}_2\text{R}, \text{CN}, \text{NO}_2, \text{SO}_2\text{R}$

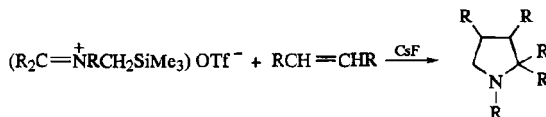
TL 34 7301 (1993); 35 7439 (1994)

 $\text{X} = \text{COR}, \text{CO}_2\text{R}$

SL 217 (1994)

 $\text{X}, \text{Y} = \text{H}, \text{CO}_2\text{R}; \text{CO}_2\text{R}, \text{CO}_2\text{R}; \text{CONMeCO}$

TL 23 2589 (1982)

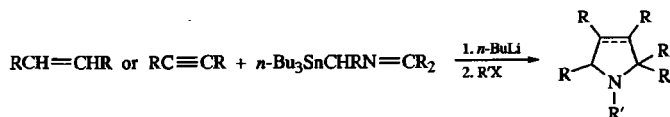


JACS 101 6452 (1979); 102 7993 (1980)

TL 24 4303 (1983); 29 5325 (1988); 30 4443, 4447, 6573 (1989)

JOC 48 1554 (1983)

Chem Rev 86 941 (1986) (review)



alkenes

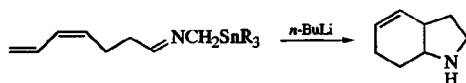
TL 29 761 (1988) (inter- and intramolecular)

JOC 57 6354 (1992); 59 5662 (1994) (intra-
molecular)JACS 114 1329 (1992); 117 12336 (1995) (intra-
molecular)

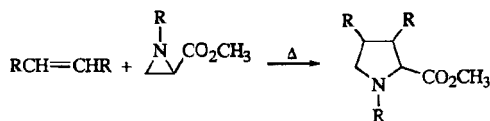
alkynes

JACS 114 1329 (1992)

JOC 57 6354 (1992)



TL 35 9172 (1994)



JACS 89 1753 (1967); 109 5523 (1987) (intramolecular); 115 10742 (1993)

Angew Int 8 602 (1969)

CC 1187, 1188 (1971)

BSCF 709 (1974)

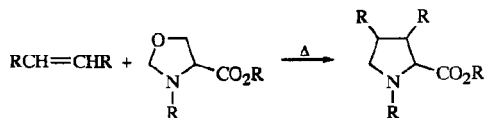
Compt Rend C 288 265 (1979)

JOC 50 2309 (1985); 53 1882 (1988); 56 3210 (1991) (intramolecular); 57 7056 (1992) (intramolecular); 58
4945 (1993) (intramolecular); 59 4 (1993) (chiral)

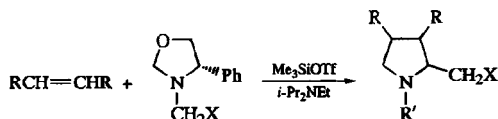
CC 1204 (1988) (intramolecular)

Heterocycles 29 1473 (1989) (intramolecular)

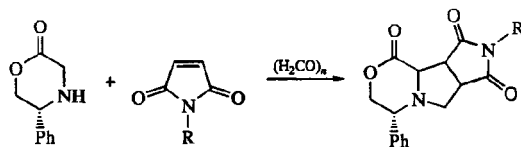
TL 35 8605 (1994)



TL 28 2973 (intramolecular), 2975 (1987)

X = CN, CO₂R

TL 30 5133 (1989); 32 7531 (1991)



molecular sieves

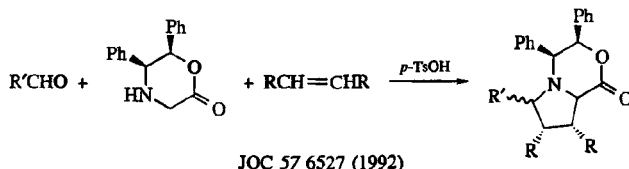
Tetr Asym 2 169, 997, 1343 (1991)

TL 34 537 (1993)

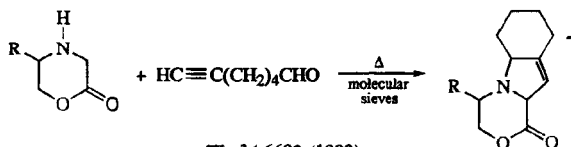
SL 925 (1994)

 MgBr_2

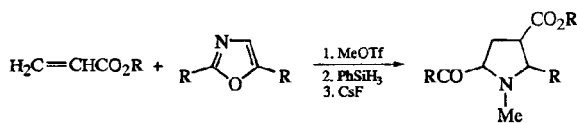
SL 777 (1993)



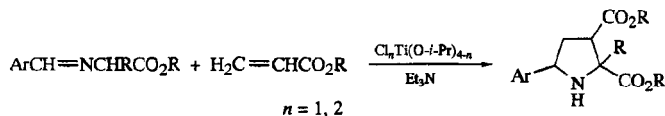
JOC 57 6527 (1992)



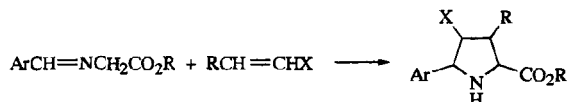
TL 34 6603 (1993)



JACS 108 6433 (1986); 110 3238 (1988)

 $n = 1, 2$

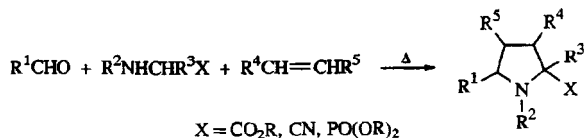
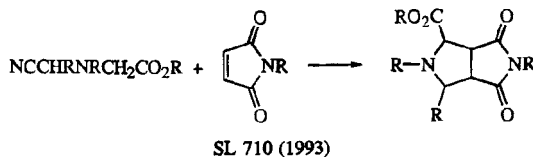
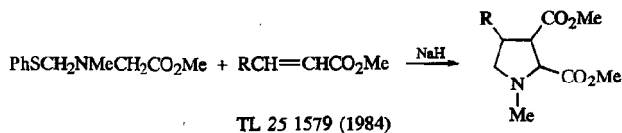
TL 30 4727 (1989)

 $\text{X} = \text{COR}, \text{CO}_2\text{R}, \text{NO}_2$

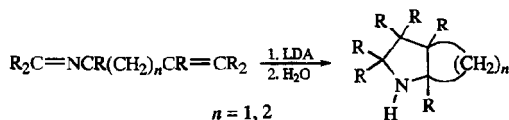
review

"Advances in Cycloadditions," Ed. D. P. Curran, JAI Press, Greenwich CT/London (1993), Vol 3, pp 99-204

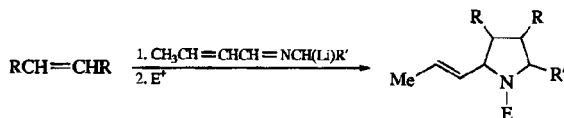
base	Tetr 44 557 (1988) TL 31 3633, 6569 (1990)
LDA, MeOH	JOC 56 4473 (1991)
LiBr, Et ₃ N	Tetr 44 557 (1988) JOC 53 1384 (1988) TL 36 2511 (1995)
LiBr, DBU	JOC 53 1384 (1988); 56 4473 (1991); 60 5005 (1995) TL 36 2511 (1995)
AgOAc, Et ₃ N	Tetr 44 557 (1988) TL 35 4413 (1994)
AgOAc, DBU	TL 34 5707 (1993); 36 2511 (1995) JOC 60 5005 (1995)
AgNO ₃ , Et ₃ N	JACS 117 7029 (1995)



CC 109 (1978); 180, 182 (1984); 1566 (1985)
 TL 2823, 2885 (1978); 25 4613 (1984); 26 2775 (1985); 30 7017 (1989) (intramolecular); 34 537 (1993) (intramolecular)
 JOC 48 2994 (1983) (intramolecular)
 Bull Soc Chim Belg 93 593 (1984) (review)
 CL 973 (1986)
 Tetr Asym 2 169, 997, 1343 (1991)

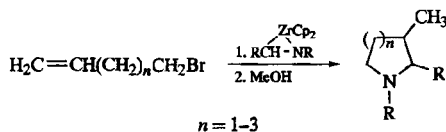


JACS 108 2769 (1986)

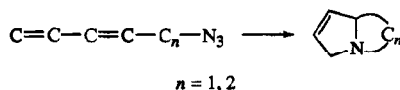


$\text{E}^+ = \text{H}_2\text{O}, \text{RX}, \text{ClCO}_2\text{R}$

TL 35 7001 (1994)



TL 36 4287 (1995)



Δ

TL 26 3523, 3527 (1985); 27 6301 (1986); 30 6661 (1989)

JACS 108 3755 (1986)

JOC 53 2094 (1988); 55 5719 (1990); 57 3977 (1992)

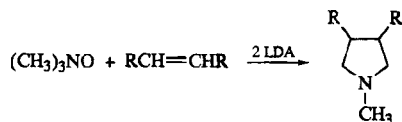
$\Delta/h\nu$

JACS 105 3273 (1983)

JOC 52 2968 (1987)

cat Cu or $\text{Cu}(\text{acac})_2$

JOC 52 3956 (1987)



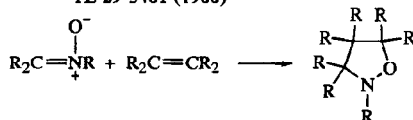
CC 31 (1983)

Heterocycles 23 653 (1985)

Can J Chem 63 725 (1985)

JOC 50 2910 (1985); 53 3808 (1988)

TL 29 3481 (1988)



Reviews:

Angew Int 16 10 (1977) (intramolecular)

A. Padwa, "1,3-Dipolar Cycloaddition Chemistry," Wiley Interscience, New York, Vol 2, Chpt 12 (1984)

Org Prep Proc Int 17 23 (1985)

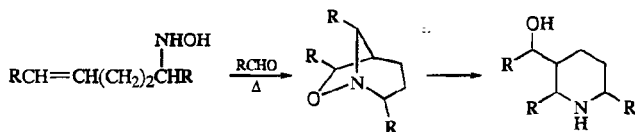
Org Rxn 36 1 (1988)

E. Breuer, H. G. Aurich, A. Nielsen, "Nitrones, Nitronates, and Nitroxides," J. Wiley, Chichester, U. K. (1989)

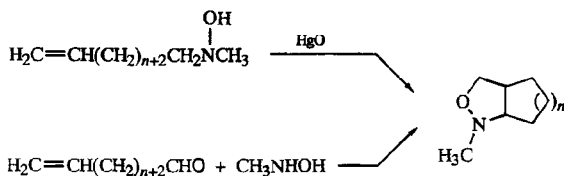
SL 1 (1993)

Recent references:

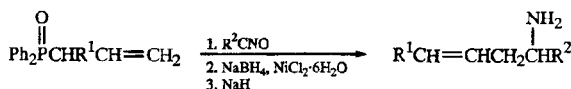
TL 29 1691, 2881 (1988); 31 6393 (1990); 32 1659, 4431 (1991) (both intramolecular); 33 3765, 7889 (1992); 34 87, 137 (1993); 35 949, 4419 (chiral catalyst), 5505 (intramolecular) (1994); 36 681, 1343 (intramolecular), 4677 (intramolecular), 5019, 7729 (intramolecular), 8665 (1995)
 JOC 53 2430, 4074, 5989 (intramolecular) (1988); 54 810, 1748, 2225, 3073, 5774 (1989); 55 1762, 1901, 3427 (1990); 56 728, 1364, 1393 (intramolecular), 2154 (intramolecular), 2775 (intramolecular), 4383, 6546 (intramolecular) (1991); 57 5666, 5834 (1992); 58 4539 (1993); 59 4375 (intramolecular), 5687 (metal catalyzed) (1994); 60 3787, 4160, 4743, 6806 (1995)
 Org Syn Coll Vol 6 670 (1988) (intramolecular)
 JACS 11 3363 (1989) (intramolecular); 117 4433 (1995)
 SL 391 (1990); 395 (1993); 279, 282, 620 (1994); 507, 935 (1995)



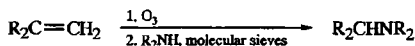
JACS 91 2820 (1969); 110 8696 (1988); 111 3363 (1989)
 Angew Int 15 123 (1976); 16 10 (1977) (both reviews)
 Helv 61 2755 (1978)
 TL 4391 (1979)
 Tetr 41 3497 (1985)
 CC 265 (1986)



JACS 81 6334 (1959)
 Angew Int 16 (1977) (review)
 TL 31 7109 (1990); 36 6713 (1995)
 SL 907 (1995)



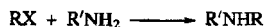
TL 32 4171 (1991)



TL 34 5309 (1993)

4. FROM ALKYL AND ARYL HALIDES OR SULFONATES

See also page 785, Section 5.



X

halide

JCS 992 (1930)
JACS 54 1499, 3441, 4457 (1932); 82 6163 (1960);
112 6696 (1990)
Org Syn Coll Vol 1 102 (1941); 2 290 (1943); 3 256
(1955); 4 466 (1963); 5 88 (1973)
TL 34 4473 (1993); 35 375 (1994)

tosylate

JACS 55 345 (1933)
JCS 694 (1955)

sulfate

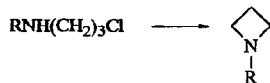
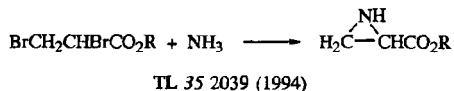
Org Syn Coll Vol 5 1018 (1973)

triflate

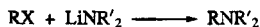
CC 1229 (1984)
JOC 50 3325 (1985); 53 3943 (1988)

phosphate

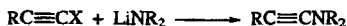
Org Syn Coll Vol 5 1085 (1973)



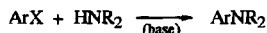
Can J Chem 67 1514 (1989)
SL 783 (1991)



Ind Eng Chem 29 1361 (1937); 33 218 (1941)



Angew 3 506 (1964); 6 767 (1967)



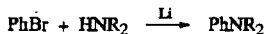
JACS 71 740 (1949)

Chem Rev 49 273 (1951) (review)

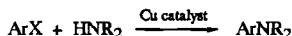
JOC 54 1476, 3436 (1989); 59 6194 (1994)

SL 803 (1991)

TL 36 4923 (1995)



JOC 58 3156 (1993)



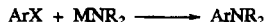
Org Syn Coll Vol 2 15 (1943); 3 307 (1955)

JACS 72 888 (1950) (intramolecular); 109 1496 (1987); 116 3279, 8877 (1994)

Tetr 40 1433 (1984) (review)

JOC 54 3091 (1989)

TL 32 39 (1991)



M = Li, Na, K

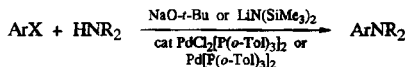
$\underline{\text{X}}$

halogen

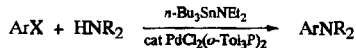
JOC 48 4397 (1983); 50 1334 (1985); 51 5157
(1986); 52 2619 (1987); 59 6194 (1994)

O_3SCF_3

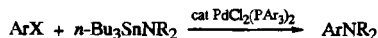
JOC 56 2045 (1991)
TL 34 7521 (1993)



TL 36 3609 (1995)



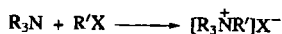
JACS 116 7901 (1994)



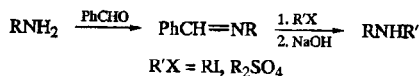
CL 927 (1983)



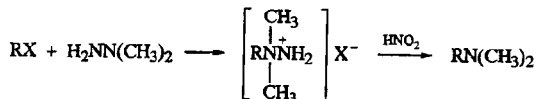
TL 34 1395 (1993)



Org Syn Coll Vol 4 85, 98, 582, 585 (1963); 5 315, 608, 825, 883, 989 (1973)

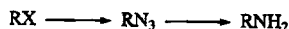


Org Syn Coll Vol 5 736, 758 (1973)

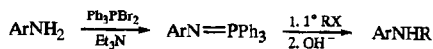


R = 1°, 2° alkyl; benzylic; propargylic

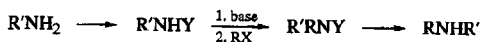
Syn Commun 12 801 (1982)



See page 815, Section 6.



Syn 295 (1980)



Y

COCF₃

JOC 39 1315 (1974)

TL 4987 (1978)

SO₂CF₃

Tetr 31 2517 (1975)

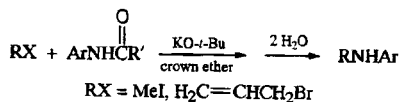
SO₂CH₂COPh

Tetr 31 2517 (1975)

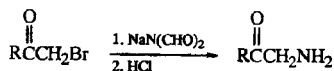
PO(OEt)₂

Angew Int 16 107 (1977)

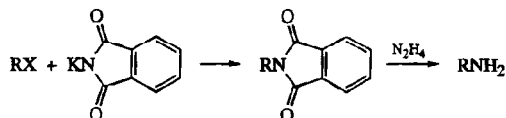
See also page 1978, Section 25.



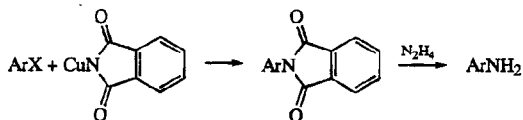
Syn Commun 9 757 (1979)



TL 30 5285 (1989)

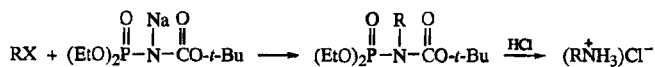


Org Syn Coll Vol 2 83 (1943)
 JACS 72 2786 (1950)
 Angew Int 7 919 (1968)
 Syn 389 (1976) (phase transfer)
 BCSJ 55 1671 (1982) (phase transfer)

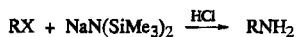


X = Br, I

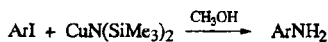
CC 578 (1969)



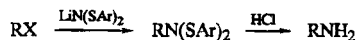
Syn 922 (1982)



Ber 94 2311 (1961); 117 1250 (1984)

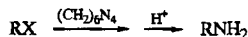


CC 256 (1974)



TL 3411 (1970)

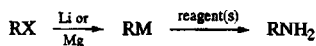
BCSJ 44 2797 (1971)



Org Rxs 8 204 (1954)

Syn 161 (1979)

JOC 58 270 (1993)

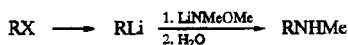


M = Li, MgX

Review: Chem Rev 89 1947 (1989)

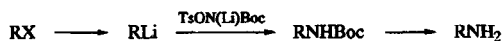
Reagent(s)

NH_2Cl	JACS 58 27 (1936); 63 1692 (1941)
NH_2OCH_3	JCS 781 (1946)
NH_2OCH_3 , CH_3Li (M = Li; R = 1°, 2°, 3° alkyl; aryl; benzylic)	JOC 47 2822 (1982) JACS 108 6016 (1986)
$\text{NH}_2\text{O}_2\text{PPh}_2$	TL 23 5399 (1982)
$\text{N}_3\text{CH}_2\text{SiMe}_3$ (R = aryl only)	CC 1322 (1983) TL 27 6193 (1986)
$\text{N}_3\text{CH}_2\text{SPh}$ / KOH or HCO_2H (R = aryl only)	JACS 103 2484 (1981)
$\text{R}^1\text{C}(\text{N}_3)=\text{CHR}^2$ (M = Li; R = aryl, benzylic)	TL 23 699 (1982)
$\text{TsN}_3/\text{LiAlH}_4$	SL 654 (1991)



R = 1°, 2°, 3° alkyl; aryl

JACS 108 6016 (1986)

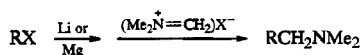


R = 1°, 2° alkyl

TL 32 2359 (1991)



JOC 60 7010 (1995)



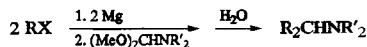
R = 1° alkyl, aryl

X

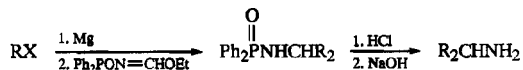
O_2CCF_3 Syn Commun 6 539 (1976)

I TL 1299 (1977); 28 3241 (1987)

For related reactions, see page 785, Section 5.

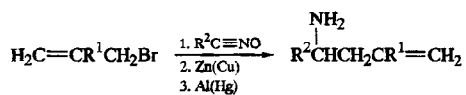


Syn 757 (1978)



R = 1° alkyl, aryl

Syn 691 (1979)



Angew Int 18 78 (1979)

5. FROM OTHER AMINES AND DERIVATIVES

1. Reduction

For imines and enamines \rightarrow amines, see page 835, Section 10.



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 3.7, p 603

H₂, cat Rh-Al₂O₃

Adv Catalysis 9 733 (1957)

H₂, cat Pd-C

JACS 113 3513 (1991)

TL 35 4759 (1994)

H₂, cat Pt

Ber 45 1471 (1912); 46 3120 (1913)

TL 34 3119 (1993)

H₂, cat PtO₂

JACS 51 887 (1929); 113 3513 (1991)

TL 36 6185 (1995)

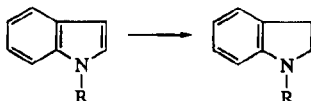
H₂, cat PtO₂, HBF₄, EtOH

CC 427 (1965)

Zn, HCl

Ber 34 3491 (1901)

JACS 51 887 (1929)

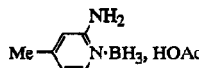


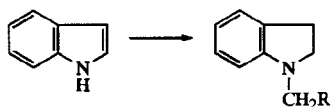
Reviews:

W. C. Sumpter and F. M. Miller, "Heterocyclic Compounds with Indole and Carbazole Systems," Ed. A. Weissberger, Interscience, New York (1954)

Chem Rev 69 785 (1969)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 3.7, p 603

H_2 , cat PtO_2 , HBF_4	CC 427 (1965) JCS C 1 (1970)
BH_3	Ann 680 69 (1964) J Med Chem 20 600 (1977)
BH_3 , CF_3CD_2H	JOC 43 2733 (1978); 52 19 (1987) CC 826 (1986)
$(CF_3CO_2)_2BH$	JOC 46 355 (1981)
CB, CF_3CO_2H	JOC 43 2733 (1978)
$BH_3 \cdot NMe_3$	Syn 508 (1974) TL 36 8693 (1995)
$BH_3 \cdot py$, HOAc	Syn 447 (1978)
$BH_3 \cdot py$, CF_3CO_2H	JOC 43 2733 (1978) J Chem Res (S) 184 (1978)
$BH_3 \cdot py$, HCl	J Chem Res (S) 212 (1977) Ann 739 (1982) J Heterocyclic Chem 23 1777 (1986)
 Me, NH_2 $N \cdot BH_3$, HOAc	J Heterocyclic Chem 23 1383 (1986)
$NaBH_3CN$, HOAc	JACS 96 7812 (1974) Syn 859 (1977) J Med Chem 21 548 (1978); 30 1555 (1987); 31 1746 (1988) Syn Commun 13 489 (1983) JOC 52 19, 1521 (1987); 53 976 (1988) JCS Perkin I 931 (1987) TL 28 3163 (1987) CC 1406 (1987)
$NaBH_3CN$, CF_3CO_2H	J Med Chem 20 600 (1977); 31 944 (1988) JOC 43 2733 (1978)
Et_3SiH , CF_3CO_2H	JOC 44 4809 (1979) JACS 109 2706 (1987) J Med Chem 30 1555 (1987); 31 1512 (1988)
Sn, HCl	JOC 44 4809 (1979)
Ni-Al, KOH	JOC 52 1043 (1987)
Zn, H_3PO_4	J Heterocyclic Chem 3 124 (1966)



NaBH₄, RCO₂H

JACS 96 7812 (1974)

NaBH₃CN, RCO₂H

Syn Commun 13 489 (1983)



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 3.6, p 579

H₂, catalyst

Adv Catalysis 14 203 (1963) (review)

H₂, cat RuO₂

JOC 26 3805 (1961)

H₂, cat Rh-C

TL 31 1537 (1990)

H₂, cat Rh-Al₂O₃

J Med Chem 32 2034 (1989)

TL 31 1537 (1990)

H₂, cat RhCl₃·3py-NaBH₄

TL 31 1537 (1990)

H₂, cat Raney Ni

JACS 56 2425 (1934)

H₂, cat PtO₂

Ber 88 789 (1955)

TL 31 1537 (1990); 35 4515 (1994)

LiHBEt₃

TL 34 7239 (1993)

Na

TL 31 1537 (1990)

Na, *n*-BuOH/H₂, cat Pd-norite

JACS 74 2895 (1952)

Sn, HCl

JACS 53 277 (1931)

Ni-Al, KOH

JOC 51 513 (1986); 57 6317 (1992)

H₂, catalyst

Adv Catalysis 14 203 (1963) (review)

BH₃·py, HOAc

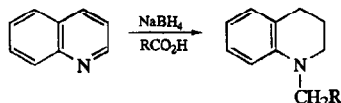
Syn 447 (1978)

NaBH₃CN, HOAc

Syn 650 (1975)

LiHBEt₃

TL 34 7239 (1993)



Syn 650 (1975)

H₂, catalyst

Adv Catalysis 14 203 (1963) (review)

BH₃·py, HOAc

Syn 447 (1978)

NaBH₃CN, HOAc

Syn 650 (1975)

LiHBEt₃

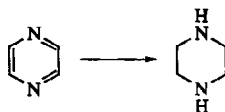
TL 34 7239 (1993)

H₂, cat PtO₂, RCHO or R₂CO

JCS C 2140 (1966)

NaBH₄, RCO₂H

Syn 650 (1975)

H₂, cat Pd-C

JOC 26 3379 (1961)

H₂, cat PtO₂

JCS 2889 (1929)

Na, EtOH

J Prakt Chem 47 439 (1893)

JCS 2889 (1929)

JOC 26 3379 (1961)

Al(Hg), EtOH

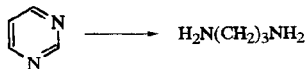
JCS 2889 (1929)

Sn, HCl

JCS 2889 (1929)

Ni-Al, KOH

JOC 52 1043 (1987)



Na, EtOH

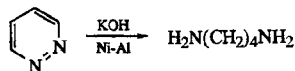
Ber 36 1915 (1903)

Ni-Al, KOH

JOC 52 1043 (1987)



Ber 34 3828 (1902)



JOC 52 1043 (1987)

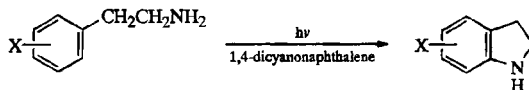
2. Alkylation on Nitrogen

See also page 779, Section 4; page 831, Section 9; and page 835, Section 10.

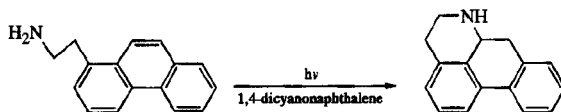


PhCHN ₂ , cat HBF ₄	TL 30 4759 (1989)
RCH=CHC(N ₂)CO ₂ R, cat Rh ₂ (OAc) ₂ (R' = RCH=CHCHCO ₂ R)	SL 1191 (1995)
[(R'O) ₃ PCH ₃]BF ₄	JOC 49 4877 (1984)
R' ₂ CuLi, O ₂	JOC 45 2739 (1980)
PhI(OTf)CH ₂ CF ₃ ; 2,4,6-collidine (R' = CH ₂ CF ₃)	TL 35 8015 (1994)
$\begin{array}{c} \text{Co}_2(\text{CO})_6 \\ \\ \text{RC}\equiv\text{C}\dot{\text{C}}\text{HR} \end{array} \text{BF}_4^-$	TL 34 2919 (1993)
$\begin{array}{c} \text{Co}_2(\text{CO})_6 \\ \\ \text{RC}\equiv\text{CCHROH} \end{array} \text{BF}_3\cdot\text{OEt}_2$	TL 36 2823 (1995)
(Ar ₂ I)X, cat Cu(OAc) ₂ (R' = Ar)	JOC 45 2127 (1980)
<i>p</i> -C ₆ H ₄ (NO ₂) ₂ (R' = <i>p</i> -C ₆ H ₄ NO ₂)	CL 31 (1986)
R' ₃ Bi, cat Cu(OAc) ₂ (R' = 1° alkyl)	TL 29 857 (1988)
Ph ₂ BiR', cat Cu(OAc) ₂ (R' = 1° alkyl)	TL 29 857 (1988)
Ph ₃ Bi, cat Cu(OAc) ₂ (R' = Ph)	TL 28 887 (1987)
Ph ₃ Bi(OAc) ₂ , cat Cu (R' = Ph)	TL 27 3615 (1986); 30 937 (1989)
Ph ₃ Bi(OAc) ₂ , cat Cu(OAc) ₂ (R' = Ph)	J Gen Chem USSR 55 413, 2232 (1985) TL 30 937 (1989)
Ph ₃ Bi(OAc) ₂ , cat Cu(O ₂ CCF ₃) ₂ (R' = Ph)	TL 30 937 (1989)
ArPb(OAc) ₃ , cat Cu(OAc) ₂ or Cu(O ₂ CCF ₃) ₂ (R' = Ar)	TL 28 3111 (1987); 30 1377 (1989)

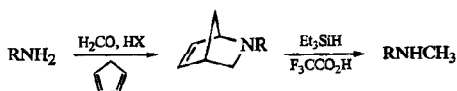
For alkylation or arylation by alkyl/aryl halides or sulfonates, see page 779, Section 4.



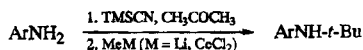
TL 31 5373 (1990)



TL 35 535 (1994)



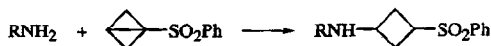
JOC 52 5746 (1987)



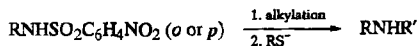
TL 34 4301 (1993)

Toc-Br = 5 α -bromo- α -tocopherol

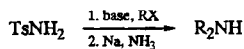
JOC 60 8120 (1995)



TL 29 1591 (1988)

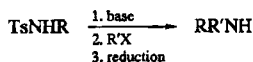


TL 36 6373 (1995)



Syn 455 (1981)

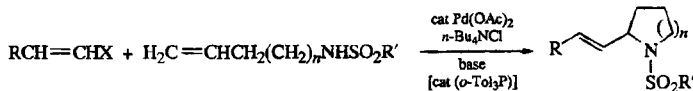
JOC 53 3521 (1988)



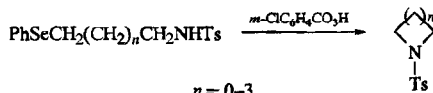
JACS 96 2268 (1974); 97 3856 (1975)

JOC 47 412, 415 (1982); 49 110 (1984); 54 2990 (1989); 58 4749 (1993)

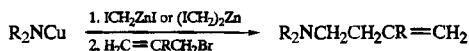
Org Syn Coll Vol 6 652 (1988)

 $n = 1, 2$; $\text{R}' = p\text{-Tol}, \text{CF}_3$; $\text{X} = \text{Br}, \text{I}, \text{OTf}$

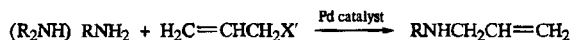
JOC 59 4172 (1994)



TL 33 4017 (1992)



JOC 58 2694 (1993)



Reviews:

Tetr 33 2615 (1977)

J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer Verlag, Berlin (1980)

R. F. Heck, "Palladium Reagents in Organic Synthesis," Academic Press, London (1985)

X

Cl

TL 24 2745 (1983)

Org Syn Coll Vol 8 9 (1993)

O₂CR

TL 3817, 3821 (1970); 3733 (1975); 24 2745 (1983);

31 1743 (1990) (chiral catalyst); 34 4193 (1993)

BCSJ 45 230 (1972)

JACS 98 8516 (1976) (intramolecular); 100 3930

(1978); 111 6301 (1989) (chiral)

JOC 44 3451 (1979); 46 3479 (1981); 49 4738

(1984); 54 2726 (1989); 58 6826 (1993); 59 5633

(1994)

Can J Chem 59 889 (1981)

Organomet 2 1625 (1983)

CC 107 (1984)

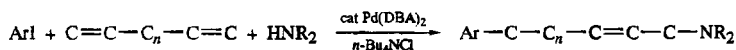
SL 715 (1992)

O₂COR

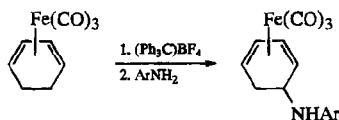
TL 32 2025 (1991); 34 5919 (1993)

O₂P(OR)₂

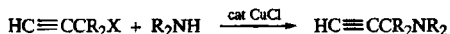
TL 23 5549 (1982)

 $n = 1, 2, 6, 10$

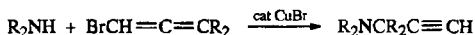
JOC 59 8107 (1994)



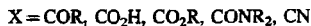
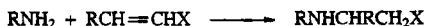
SL 371 (1992) (review)

 $X = OAc, OPO(OEt)_2$

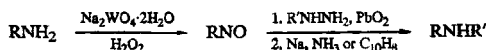
JOC 59 2282 (1994)



TL 32 7471 (1991)



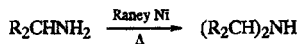
See page 761, Section 3.



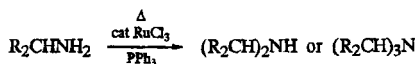
JOC 50 5391 (1985)

Org Syn 65 166 (1987)

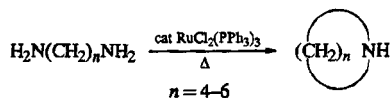
Org Syn Coll Vol 8 93 (1993)



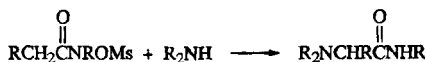
Syn 70 (1979)



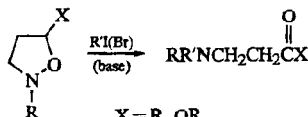
JOC 46 1759 (1981)



JOC 46 1759 (1981)



JOC 58 2355 (1993)



TL 29 5949 (1988)

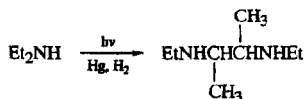
3. Alkylation on Carbon

For reviews of metalation and electrophilic substitution of amine derivatives adjacent to nitrogen, see:

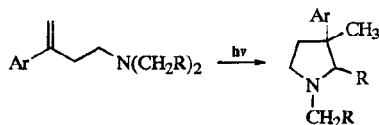
Chem Rev 84 471 (1984)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.2, p 65

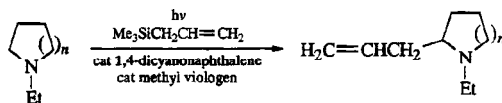
See page 1778, Section 4, for alkylation on carbon next to the nitrogen of an amide, urethane or phosphorus derivative.



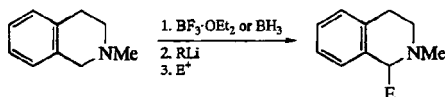
JACS 113 2233 (1991)



JOC 57 3037 (1992)

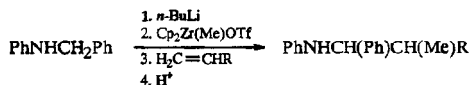
 $n = 1, 2$

TL 33 5107 (1992)

 $E^+ = RX, RCHO, R_2CO, R_3SiCl$

TL 32 3221 (1991); 36 8697 (1995)

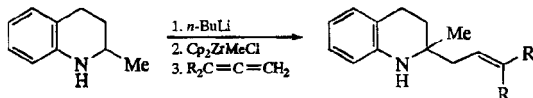
CC 568 (1991); 1327 (1994)



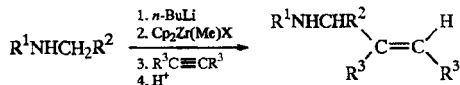
JACS 113 2321 (1991) (chiral)

SL 143 (1992)

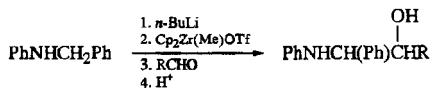
TL 35 2431 (1994)



SL 143 (1992)

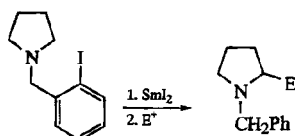


See page 440, Section 2.15.

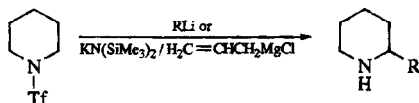


JACS 113 2321 (1991) (chiral)

SL 143 (1992)

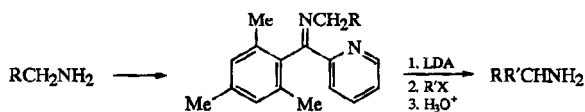


JOC 57 793 (1992)

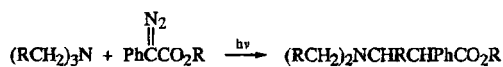


$R = n\text{-Bu}, i\text{-Bu}, \text{CH}_2\text{CH}=\text{CH}_2$

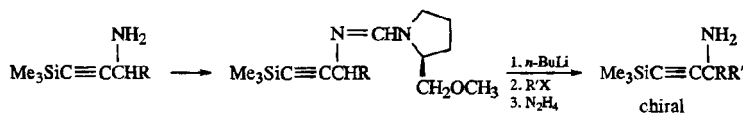
TL 36 6063 (1995)



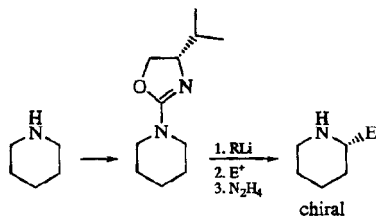
TL 30 5853 (1989)



TL 30 6353 (1989)



Ann 1668 (1983)

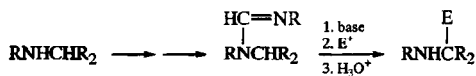


$E^+ = RX, RCHO$

JOC 51 3076 (1986); 53 5381 (1988); 54 175, 3002 (1989); 56 1564 (1991)

JACS 109 1265 (1987) (mechanism); 111 2211 (1989)

TL 29 301 (1988); 31 3711 (1990); 33 2945 (1992)



Reviews:

Lectures in Heterocyclic Chemistry 7 75 (1984)

T. K. Highsmith, A. I. Meyers, "Advances in Heterocyclic Natural Product Synthesis," Ed. W. H. Pearson, JAI Press, Greenwich, CT (1991) (chiral)

JACS 102 7125 (1980); 105 117 (1983); 106 3270 (1984); 107 7974 (1985) (chiral); 109 1262 (1987) (chiral, mechanism); 110 4778 (1988) (chiral); 113 2789 (1991) (chiral); 114 8483 (1992) (chiral); 115 6652 (1993)

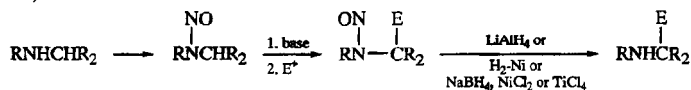
TL 22 5115, 5119 (1981); 26 3291 (1985) (chiral); 27 1465 (1986) (chiral); 30 43, 47, 911, 1909, 5945 (1989); 31 417, 2157, 2813 (1990); 32 5501, 5505, 5509 (1991) (all chiral); 33 5693 (1992); 36 5873, 5877 (1995) (both chiral)

JOC 51 3108 (1986) (chiral); 54 5632 (1989); 55 4218, 5659 (1990) (both chiral); 56 2091 (chiral), 2751, 2960 (chiral), 6873 (chiral) (1991); 57 3444, 3819 (chiral), 4732 (chiral) (1992); 58 6538 (1993)

Tetr 43 5095 (1987) (chiral)

Org Syn Coll Vol 8 573 (1993) (chiral)

SL 551 (1993)



Angew Int 14 15 (1975)

Ber 108 1293 (1975); 110 1852 (1977); 111 2630 (1978)

Can J Chem 53 2473 (1975)

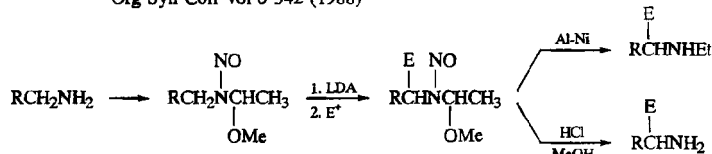
Syn 548 (1976); 423 (1979); 741 (1980) (reduction)

Org Syn 58 113 (1978)

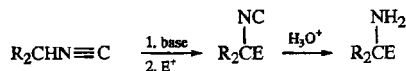
Chem Rev 78 275 (1978) (review)

JCS Perkin I 579 (1979)

Org Syn Coll Vol 6 542 (1988)

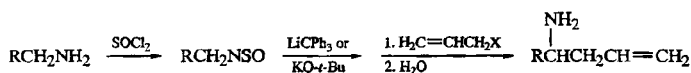


JOC 48 2388 (1983)

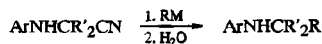


Angew Int 10 491 (1971)

Ann 183 (1976); 40 (1977)



JACS 100 2894 (1978)

RM

MeLi

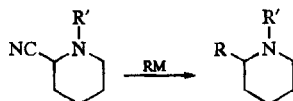
TL 34 4301 (1993)

ArLi (Ar = heterocycle)

TL 29 6827 (1988)

MeCeCl₂

TL 34 4301 (1993)

RM

RMgX (R = 1° alkyl, aryl)

Bull Soc Chim Belg 33 467 (1924)

BSCF 3803 (1968)

TL 28 741 (1987); 30 4613 (1989)

JOC 58 6451 (1993)

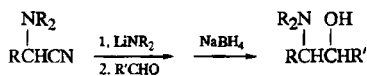
RX, Na, NH₃

SL 44, 878 (1991)

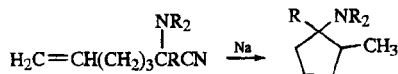
LDA/RX/Li-NH₃ or Na-NH₃ or NaBH₄

TL 23 3369 (1982); 28 547 (1987)

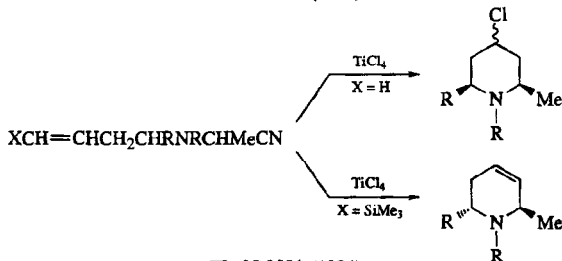
SL 878 (1991)



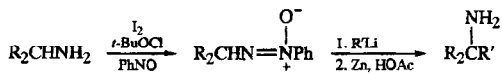
TL 771 (1979)



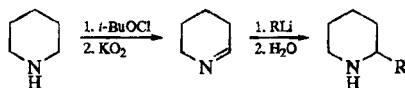
TL 30 4203 (1989)



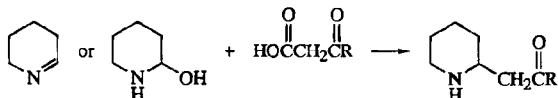
TL 35 3581 (1994)



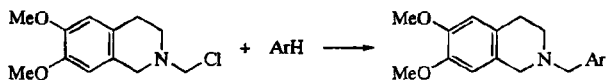
JCS Perkin I 2030 (1979)



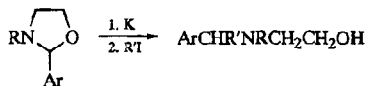
JOC 45 1515 (1980)



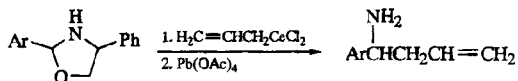
Ann 626 123 (1959)



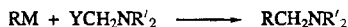
SL 617 (1990)



JOC 58 6707 (1993)



SL 636 (1990)

RMYR'RLi, (*i*-Pr₂NH) (R = 1°, 3° alkyl; aryl)

RS

alkyl

JOC 59 7 (1994)

RLi; RMgX (R = 1°, 2°, 3° alkyl; vinyl; Ph); RCeX₂

-oxazolidine-

TL 35 7489 (1994)

CH₃CH₂CH=CHCH₂M (M = Li, MgX, ZnX)*n*-BuO, *n*-BuS

alkyl

BSCF 2544 (1968)

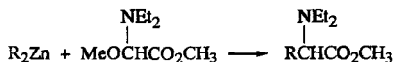
CH₃CH=CHCH₂M (M = Li, MgX, AlX₂, ZnX, Cu);
RC≡CCH₂M (M = MgX, AlX₂, ZnX)*n*-BuO

alkyl

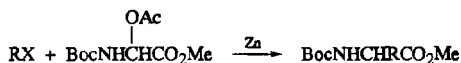
JOMC 198 1 (1980)

RM	Y	R'	RM + YCH ₂ NR' ₂ → RCH ₂ NR' ₂ (continued)
RC≡CLi, BF ₃ ·OEt ₂	OR	alkyl	TL 35 5003 (1994)
RMgBr (R = 1° alkyl)	OR	alkyl	BSCF II 148 (1983) TL 28 547 (1987); 29 6949 (1988); 32 1443 (1991); 33 235 (1992) JOC 54 5558 (1989); 58 6451 (1993) SL 669 (1990)
RMgX (R = 1°, 2° alkyl; aryl)	OR	alkyl	SL 763 (1990) TL 33 867 (1992)
RMgBr (R = Me, PhCH ₂ , allyl, propargyl, alkynyl, aryl)	MeO, <i>c</i> -C ₆ H ₁₃ O	SiMe ₃	Angew Int 23 53 (1984)
RMgX (R = 1° alkyl, allyl, benzyl, aryl)	<i>n</i> -BuO	alkyl	JCS 123 532 (1923)
RMgX (R = 1°, 2° alkyl; allyl; benzyl)	<i>n</i> -BuO	alkyl	TL 30 7383 (1989)
RMgX (R = 1°, 2° alkyl; allyl; benzyl; aryl; vinylic; alkynyl)	MeO	alkyl	TL 31 4723 (1990)
RMgX (R = 1°, 2°, 3° alkyl; allyl; benzyl)	EtO	alkyl	JACS 62 1450 (1940)
RMgX (R = 1°, 2° alkyl; benzylic; aryl)	<i>n</i> -BuO	alkyl	JACS 77 1098 (1955)
ArMgX	OR	alkyl	SL 669 (1990)
RMgX (R = 1°, 2° alkyl; allylic; aryl)	PhS	alkyl	JOC 32 272 (1967)
RMgX (R = allyl; benzyl)	Cl	alkyl	Arch Pharm 305 10 (1972)
H ₂ C=CHMgX, PhCeCl ₂	—oxazolidine—		TL 35 7533 (1994)
RMgX (R = 1° alkyl, aryl CH ₂ CO ₂ - <i>i</i> -Bu, vinylic), EtO ₂ CCH ₂ ZnBr, Et ₂ NCOCH ₂ ZnBr, (EtO ₂ C) ₂ CRZnBr (R = H, Me)	<i>n</i> -BuO	alkyl	BSCF II 395 (1982)
RC≡CMgBr	<i>n</i> -BuO	alkyl	BSCF II 21 (1983)
RC≡CMgX, Et ₂ NCOCH ₂ ZnBr, (CH ₃ CH=CHCH ₂) _n AlBr _{3-n} or (H ₂ C=C=CMe) _n AlBr _{3-n}	OR	<i>i</i> -Pr, SiMe ₃	TL 28 1659 (1987)
RMgX (R = 1° alkyl, aryl), BF ₃ ·OEt ₂	MeO	CO ₂ R	TL 31 6385 (1990)
BF ₃ ·OEt ₂ or R ₃ SiOTf/RMgX (R = 1°, 2° alkyl)	OR	alkyl	JOC 59 3769 (1994)
<i>E</i> -RCH=CHAl(<i>i</i> -Bu) ₂ , R ₂ CuLi (R = 1° alkyl, vinylic)	<i>n</i> -BuO, <i>i</i> -BuO, PhS	alkyl	TL 21 3763 (1980)

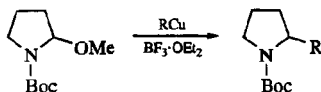
Et_2AlCN	OR	alkyl	SL 45 (1992)
$\text{RCH}=\text{CHCH}_2\text{SiMe}_3$, TiCl_4	MeO	Ts CO_2R	TL 33 3791 (1992) JOC 55 4118 (1988)
$n\text{-Bu}_3\text{SnAr}$	Cl	alkyl	SL 617 (1990)
RZnX ($\text{R} = 1^\circ, 2^\circ$ alkyl; allyl; vinyl)	PhS	alkyl	TL 31 2889 (1990)
$\text{RO}_2\text{CCH}_2\text{ZnBr}$	OR	alkyl	TL 33 2895 (1992)
R_2Zn	OR	R	TL 33 4743 (1992)



JOMC 256 193 (1983)

RX = allylic, benzylic or propargyl halide; α -halo ester

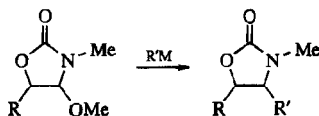
TL 35 3669 (1994)



Tetr 47 573 (1991)

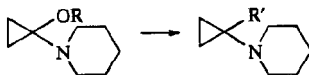
TL 35 6105 (1994)

JOC 60 454, 5011 (1995)



$\text{R}'\text{M} = \text{R}_2\text{CuLi} \cdot \text{BF}_3 \cdot \text{OEt}_2$, $\text{R}_3\text{Cu}_2\text{Li} \cdot \text{BF}_3 \cdot \text{OEt}_2$, $\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3\text{-TiCl}_4$,
 $n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2\text{-BF}_3 \cdot \text{OEt}_2$ or Me_3SiOTf

SL 339 (1991)



R

Reagent(s)

H

TiCl_4 ; ArH, enol silane or
 $(\text{RO}_2\text{C})_2\text{CH}_2$ [$\text{R}' = \text{Ar}$,
 CH_2COR or $\text{CH}(\text{CO}_2\text{R})_2$]

TL 23 785 (1982)

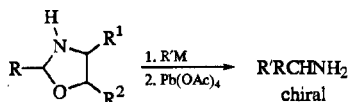
 SiMe_3

$\text{R}'\text{MgX}$ ($\text{R} = 1^\circ$ alkyl, aryl,
 vinylic)

TL 23 785 (1982)

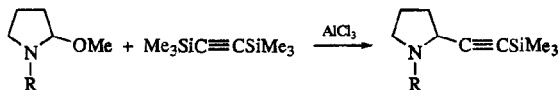
H or SiMe_3 KCN , HOAc ($\text{R}' = \text{CN}$)

TL 23 1413 (1982)



M = Li, MgX, Cu·BF₃, CeX₂; R = aryl, vinylic

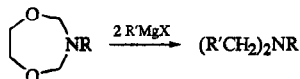
JOC 56 1340 (1991); 57 1237 (1992)



TL 31 719 (1990)



Syn 757 (1978)



TL 24 1597 (1983)



R = allylic, benzylic, propargylic, CHRCO₂R

TL 35 1561 (1994)



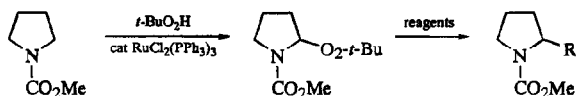
R'M

R₄Pb, TiCl₄ TL 30 5611 (1989)

RCu, (BF₃) TL 31 1775 (1990)

R₂CuLi, BF₃·OEt₂ TL 30 5611 (1989)

R₂Zn, TiCl₄ TL 30 5611 (1989)



R

R

CH₂CH=CH₂

CH₂COR

CH(CN)CO₂R

CN

Reagents

RMgX, TiCl₄

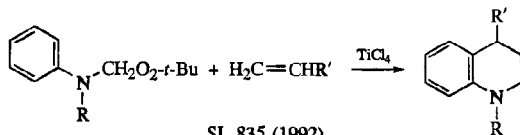
H₂C=CHCH₂SiMe₃, TiCl₄

H₂C=CROSiMe₃, TiCl₄

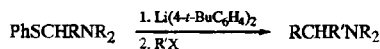
H₂C(CN)CO₂R, TiCl₄, Et₃N

Me₃SiCN, TiCl₄

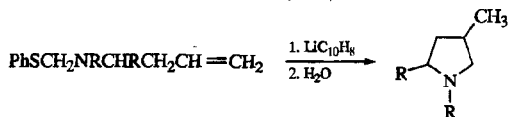
TL 31 7475 (1990)



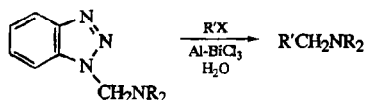
SL 835 (1992)



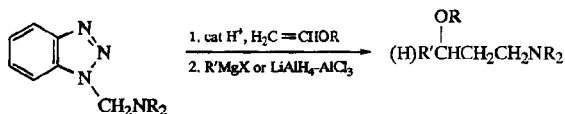
TL 32 1975 (1991)



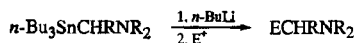
JACS 111 2981 (1989)


$$R' = \text{Me, PhCH}_2, \text{H}_2\text{C}=\text{CHCH}_2, \text{HC}\equiv\text{CCH}_2$$

TL 32 4247 (1991)

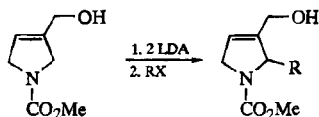


JOC 57 4932 (1992)

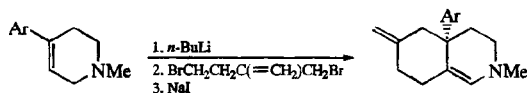

$$E^+ = \text{MeOH, Me}_2\text{SO}_4, \text{RCHO, R}_2\text{CO, RCOCl, CO}_2, \text{ClCO}_2\text{R, ROCO}_2\text{R, R}_3\text{SnCl}$$

TL 34 51 (1993)

JOC 60 5763 (1995)

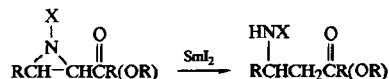


JOC 48 1129 (1983)

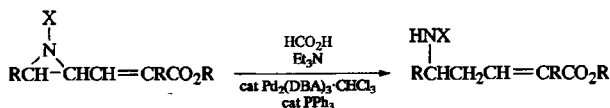


TL 23 285 (1982)

4. Ring Opening

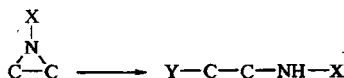
X = CPh₃, Ac, CO₂R, Ts

JOC 60 6660 (1995)



X = Ts, Boc

SL 64 (1995)





Reviews: Angew Int 1 528 (1962); 33 599 (1994)

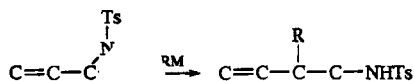
X	Y	Reagent(s)	
H	F	HF	J Chem Res (S) 210 (1980)
		HF, py	TL 3247 (1978); 2681 (1979)
	Cl	HCl	TL 31 1989 (1990)
			Rec Trav Chim 111 16 (1992)
	OR	ROH, H ₂ SO ₄	JOC 60 2514 (1995)
		ROH, BF ₃ ·OEt ₂	Syn 288 (1992)
	SR	RSH	Tetr 43 3881 (1987)
		RSH, Et ₃ N	JOC 60 2514 (1995)
		RSH, BF ₃ ·OEt ₂	JOC 53 3154 (1988); 60 790 (1995)
			TL 30 4881 (1989)
R	N ₃	RSH, Mg(ClO ₄) ₂	Rec Trav Chim 111 16 (1992)
		NaN ₃ ; NH ₄ Cl,	JOC 60 2514 (1995)
		Mg(ClO ₄) ₂ or	JOC 60 2514 (1995)
	3-indolyl	Zn(OTf) ₂	
		indole, BF ₃ ·OEt ₂	Rec Trav Chim 111 16 (1992)
	H	H ₂ , cat Pd(OH) ₂	TL 36 8431 (1995)
		HF, py	TL 3247 (1978)
		Li ₂ NiBr ₄	JOC 54 5324 (1989)
			TL 36 8015 (1995)
	OR	ROH, BF ₃ ·OEt ₂	Syn 288 (1992)
	SPh	NaSPh	JOC 54 5324 (1989)
	SCN	KSCN, BF ₃ ·OEt ₂	TL 36 8015 (1995)
	NHR	RNH ₂ , cat Yb(OTf) ₃	TL 35 7395 (1994)
	NR ₂	R ₂ NH	TL 23 5021 (1982)

	PO(OMe) ₂	P(OMe) ₃ , PhCO ₂ H or PhOH	BCSJ 343 (1979)
	R	R ₂ CuLi, BF ₃ ·OEt ₂	TL 26 1153 (1985); 27 4157 (1986) JOC 54 5324 (1989)
COR	Cl	HCl	BCSJ 55 174 (1982) Rec Trav Chim 111 59 (1992)
	I	HI	BCSJ 55 174 (1982)
	O ₂ CR	RCO ₂ H	Rec Trav Chim 111 59 (1992)
	SR	RSH, BF ₃ ·OEt ₂	Rec Trav Chim 111 59 (1992) JOC 60 2035 (1995)
	NHR, NR ₂	RNH ₂ , R ₂ NH	J Med Chem 8 107 (1965) BCSJ 53 283 (1980)
	CR ₂ COR	NaCR ₂ COR	Syn 392 (1986)
	CR ₂ CO ₂ H	LiCR ₂ CO ₂ Li	Syn 395 (1986)
	CR ₂ CN	LiCR ₂ CN	TL 23 5021 (1982)
	C(=PPh ₃)CO ₂ R	Ph ₃ P=CHCO ₂ R	JOC 35 444 (1970) CC 153 (1987)
	CH(COCH ₃) ₂	NaCH(COCH ₃) ₂	J Heterocyclic Chem 28 1757 (1991)
	CH(COCH ₃)CO ₂ R	NaCH(COCH ₃)CO ₂ R	J Heterocyclic Chem 28 1757 (1991)
	CR(CO ₂ R) ₂	NaCR(CO ₂ R) ₂	J Heterocyclic Chem 28 1757 (1991)
	CH(CN)CO ₂ R	LiCH(CN)CO ₂ R	TL 23 5021 (1982)
	CH(CN) ₂	NaCH(CN) ₂	J Heterocyclic Chem 28 1757 (1991)
	fluorene	fluorenyl Li	TL 23 5021 (1982)
	3-indolyl	indole, BF ₃ ·OEt ₂	Rec Trav Chim 111 59 (1992) JOC 59 434 (1994)
		indole, Zn(OTf) ₂	TL 30 4073 (1989)
CO ₂ R	Cl	HCl	JOC 60 2514 (1995)
		NaCl	JOC 60 2514 (1995)
		TiCl ₄	JOC 60 2514 (1995)
	Br	LiBr, BF ₃ ·OEt ₂	JOC 60 2035 (1995)
		Li ₂ NiBr ₄	JOC 54 5324 (1989) TL 36 8015 (1995)
	O ₂ CR	RCO ₂ H	JOC 54 1940 (1989) Rec Trav Chim 111 59 (1992)
		RCO ₂ H, BF ₃ ·OEt ₂	JOC 60 2035 (1995)
	OR	ROH, H ₂ SO ₄	JOC 60 2514 (1995)
		ROH, LiClO ₄	JOC 60 2514 (1995)
		ROH, BF ₃ ·OEt ₂	BCSJ 55 3049 (1982) JOC 60 2035 (1995)
	OTs	TsOH	JOC 60 2514 (1995)
	SH	NaSH·H ₂ O	JOC 54 5324 (1989)
	SR	RSH, LiClO ₄	JOC 60 2514 (1995)
		RSH, BF ₃ ·OEt ₂	BCSJ 56 520 (1983) TL 24 1133 (1983) Rec Trav Chim 111 59 (1992)
		RSH, Et ₃ N	JOC 60 2035 (1995)
	SPh	NaSPh	JOC 60 2514 (1995) SL 527 (1992)
			TL 35 1201 (1994)
	SCOR	RCOSH, BF ₃ ·OEt ₂	BCSJ 55 3878 (1982)

<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
CO ₂ R (cont'd)	NHR	RNH ₂ , cat Yb(OTf) ₃	TL 35 7395 (1994)
	NR ₂	R ₂ NH	JOC 60 2514 (1995)
		R ₂ NH, LiClO ₄	JOC 60 2514 (1995)
		R ₂ NH, cat Yb(OTf) ₃	TL 35 7395 (1994)
	N ₃	NaN ₃	JOC 54 5324 (1989); 60 2514 (1995)
		NaN ₃ , NH ₄ Cl	JOC 60 2514 (1995)
		NaN ₃ , LiClO ₄	JOC 60 2514 (1995)
		NaN ₃ , BF ₃ ·OEt ₂	JOC 54 5324 (1989)
		NaN ₃ , <i>n</i> -Bu ₄ N ⁺	TL 35 1201 (1994)
		or (H ₂ N) ₂ C=NH ₂	
		LiCR ₂ CN	TL 23 5021 (1982)
	CR ₂ CN	LiCPh ₃	TL 26 1153 (1985)
	CPh ₃	RMgX	JOC 44 2788 (1979)
	R	RMgX, cat CuBr·SMe ₂	TL 32 1897 (1991)
		RCu·BF ₃	JOC 44 2788 (1979)
		R ₂ CuLi	JOC 44 2788 (1979); 54 5324 (1989)
			TL 27 4157 (1986)
			Chem Pharm Bull 38 564 (1990)
	3-indolyl	indole, BF ₃ ·OEt ₂	TL 30 4073 (1989)
		indole, Zn(OTf) ₂	SL 235 (1995)
	CN	NaCN	SL 235 (1995)
		Et ₂ AlCN	SL 235 (1995)
		Me ₃ SiCN, cat Yb(CN) ₃	SL 235 (1995)
CONHR	CH(CN)CO ₂ R	LiCH(CN)CO ₂ R	TL 23 5021 (1982)
CONR ₂	CR ₂ COR	NaCR ₂ COR	Syn 392 (1986)
	CR ₂ CO ₂ H	LiCR ₂ CO ₂ Li	Syn 395 (1986)
SO ₂ Ar	H	<i>i</i> -Bu ₂ AlH	Tetr 48 6069 (1992)
		LiAlH ₄	Tetr 48 6069 (1992)
		NaH ₂ Al(OCH ₂ -CH ₂ OCH ₃) ₂	Tetr 48 6069 (1992)
	F	<i>n</i> -Bu ₄ NF	JOC 54 5324 (1989)
		HCl	Rec Trav Chim 111 59 (1992)
			JOC 60 2514 (1995)
			JOC 60 2514 (1995)
			TL 28 3341 (1987)
	Cl	NaCl	JOC 54 5324 (1989)
		Li ₂ CuCl ₄	TL 28 3341 (1987)
			JOC 54 5324 (1989)
			TL 28 3341 (1987)
			JOC 54 5324 (1989)
	Br	LiBr, BF ₃ ·OEt ₂	TL 31 1903 (1990)
		MgBr ₂	JOC 54 5324 (1989)
		<i>n</i> -Bu ₄ NBr	TL 28 3341 (1987)
		Li ₂ NiBr ₄	JOC 54 5324 (1989)
			TL 31 1903 (1990)
	I	MgI ₂	Rec Trav Chim 111 59 (1992)
		HCO ₂ H	JOC 53 4616 (1988)
		NaOAc	SL 661 (1992)
		ROH, BF ₃ ·OEt ₂	JACS 112 2368 (1990)
		NaOR	JOC 58 4681 (1993)
	O ₂ CH	ArOH, K ₂ CO ₃	TL 28 3341 (1987)
	OAc	NaSH, H ₂ O	JOC 54 5324 (1989)
	OR		JOC 60 2514 (1995)
	OAr		
	SH		
	SR	RSH, LiClO ₄	

	RSH, BF ₃ ·OEt ₂	Rec Trav Chim 111 59 (1992)
	RSH, Et ₃ N	JOC 60 2514 (1995)
	NaSR	TL 28 3341 (1987)
		JOC 54 5324 (1989)
NHR, NR ₂	RNH ₂ , R ₂ NH	TL 23 5021 (1982); 36 4955 (1995)
		JOC 47 412 (1982); 60 2514 (1995)
	R ₂ NH, LiClO ₄	JOC 60 2514 (1995)
	RNH ₂ or R ₂ NH, cat Yb(OTf) ₃	TL 35 7395 (1994)
N ₃	NaN ₃	TL 28 3341 (1987); 31 1903 (1990)
		JOC 54 5324 (1989); 60 2514 (1995)
	NaN ₃ , NH ₄ Cl	JOC 60 2514 (1995)
	NaN ₃ , LiClO ₄	JOC 60 2514 (1995)
	NaN ₃ , BF ₃ ·OEt ₂	TL 28 3341 (1987)
		JOC 54 5324 (1989)
	Me ₃ SiN ₃	Rec Trav Chim 111 59 (1992)
CN	NaCN	JACS 117 9069 (1995)
	KCN	TL 36 151 (1995)
	Me ₃ SiCN, cat M(CN) ₃ (M = Yb, Y, Ce)	TL 31 6379 (1990)
	Me ₂ C(OH)CN, cat La(O- <i>i</i> -Pr) ₃	CL 975 (1993)
CH ₂ COCH ₂ CO ₂ R	CH ₂ COCHCO ₂ R	SL 764 (1993)
CHRCO ₂ R	LiCHRCO ₂ R	JOC 58 5019 (1993) (intramolecular)
CR ₂ CN	LiCR ₂ CN	TL 23 5021 (1982)
CR(CN)CO ₂ R	LiCR(CN)CO ₂ R	TL 23 5021 (1982)
CH(CO ₂ R) ₂	LiCH(CO ₂ R) ₂	TL 23 5021 (1982)
		JOC 54 1940 (1989)
C(=PPh ₃)CO ₂ R	Ph ₃ P=CHCO ₂ R	CC 153 (1987)
CH ₂ PO(OEt) ₂	LiCH ₂ PO(OEt) ₂	JOC 54 906 (1989)
CH ₂ SO ₂ Ph	LiCH ₂ SO ₂ Ph	SL 513 (1993)
		SL 675 (1993)
fluorenyl	fluorenyl Li	TL 23 5021 (1982)
CH(OTHP)-	LiCH(OTHP)-	JOC 44 2788 (1979)
C(Me)=CH ₂	C(Me)=CH ₂	
C≡CR	LiC≡CR	TL 28 3341 (1987)
		JOC 54 5324 (1989)
R	RMgX	Helv 60 205 (1977)
		JOC 44 2788 (1979); 54 1940, 5324 (1989)
		TL 28 3341 (1987)
		JACS 117 2943 (1995)
	RMgX, cat	CC 1852 (1989)
	CuBr·SMe ₂	Tetr 49 6309 (1993)
	R ₃ Al	Tetr 48 6069, 6079 (1992)
	R ₂ CuLi	JOC 44 2788 (1979); 54 5324 (1989); 60 2044 (1995)
		TL 27 4157 (1986); 28 3341 (1987); 31 1903 (1990); 34 7421 (1993)
		Tetr 44 619 (1988); 48 6069 (1992)

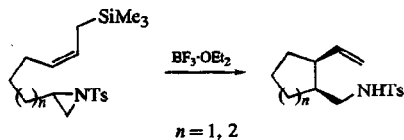
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
SO ₂ Ar (<i>cont'd</i>)	R (<i>cont'd</i>)	R ₂ CuLi, BF ₃ ·OEt ₂	TL 28 3341 (1987)
		R ₂ Cu(CN)Li ₂	TL 28 3341 (1987); 36 151 (1995) JOC 54 5324 (1989); 60 2044 (1995) Tetr 48 6069 (1992); 49 6309 (1993) JACS 117 3643 (1995)
	Ar	RCu(CN)Li	TL 34 7421 (1993)
		ArH, AlCl ₃	JOC 54 193 (1989) TL 35 2739 (1994)
POPh ₂	I	MgI ₂	SL 145 (1994)
	SPh	LiSPh	SL 145 (1994)
	SePh	(PhSe) ₂ , NaBH ₄	SL 145 (1994)
	N ₃	NaN ₃	SL 145 (1994)
	CN	Me ₃ SiCN, Ce(CN) ₃	SL 145 (1994)
	R	RMgX, CuBr·SMe ₂	TL 35 2739 (1994)
		RMgX, cat CuBr·SMe ₂	SL 1277 (1995)
		R ₂ CuLi	SL 145 (1994)

RM

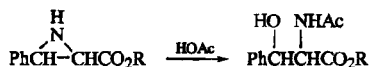
RMgX, CuI JOC 59 4037 (1994)

R₂CuLi JOC 59 4037 (1994)Ar₂Cu(CN)Li₂ JACS 117 3643 (1995)Ar₂Cu(CN)Li₂, BF₃·OEt₂ SL 1125 (1995)E⁺ = H₂O, D₂O, RX, RCHO, R₂CO, RCONR₂, RCH=NR, ROCO₂R, RSSR

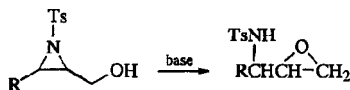
JOC 59 3210 (1994)



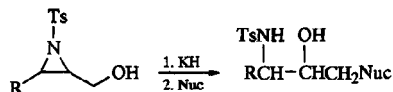
TL 36 3793 (1995)



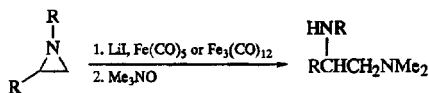
Rec Trav Chim 111 16 (1992)



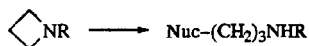
JOC 60 2044 (1995)

Nuc = $\text{X}_2\text{Cu}(\text{CN})\text{Li}_2$ (X = R, R_2N , Me_3Si , $n\text{-Bu}_3\text{Sn}$); Me_3SiCN , cat $\text{Yb}(\text{CN})_3$

TL 36 6247 (1995)



JOC 55 2531 (1990)

Nuc-H

ArOH

JOC 59 2172 (1994)

 RCO_2H , KO_2CR

J Heterocyclic Chem 6 273 (1969)

 RNH_2 , $\text{CF}_3\text{CO}_2\text{H}$ or $\text{BF}_3 \cdot \text{OEt}_2$

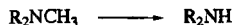
J Heterocyclic Chem 6 273 (1969)

 R_2NH , $\text{CF}_3\text{CO}_2\text{H}$ or $\text{BF}_3 \cdot \text{OEt}_2$

J Heterocyclic Chem 6 273 (1969)

5. Dealkylation

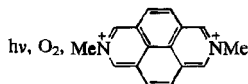
Review: Houben-Weyl, Vol XI/1, p 961

hv, KOH, cat dicyanonaphthalene, MeOH
(anilines)

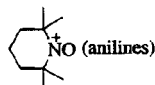
TL 31 1199 (1990)

hv, O_2 , LiClO_4 , 9,10-dicyanoanthracene

TL 30 3977 (1989)



TL 30 2927 (1989)

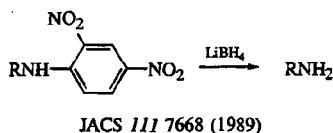
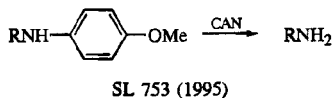


JOC 53 1278 (1988)

 ClCO_2Et , KOH

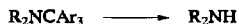
J Pharm Sci 56 976 (1967)

$\text{ClCO}_2\text{Et} / \text{H}_3\text{O}^+$	JCS C 2015 (1967) TL 57 (1971) J Med Chem 16 342 (1973)
$\text{ClCO}_2\text{CH}_2\text{CCl}_3 / \text{Zn}$	TL 1325 (1974) SL 343 (1994)
$\text{ClCO}_2\text{CH}_2\text{Ph}, \text{NaHCO}_3$	JACS 77 3104 (1955)
$\text{ClCO}_2\text{Ph}, \text{KHCO}_3$	J Med Chem 15 208 (1972)
$\text{ClCO}_2\text{Ph}, (\text{LiI}) / \text{hydrolysis}$	JCS C 2015 (1967)

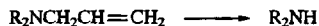


H_2 (review)	Org Rxs 7 263 (1953)
H_2 , cat Pd-C	Helv 35 1162 (1952) J Chem Res (S) 164 (1981) TL 29 631, 1391 (1988); 30 317 (1989) SL 45 (1991) JOC 60 4177, 7086 (1995)
H_2 , cat $\text{Pd}(\text{OH})_2\text{-C}$	JOC 57 6071 (1992); 60 7084 (1995) TL 34 7781 (1993); 35 5389 (1994)
H_2 , cat $\text{PdCl}_2\text{-C}$	JACS 65 1984 (1943); 72 3410 (1950); 75 5598 (1953)
H_2 , cat $\text{Pd}(\text{OH})_2$	JOC 60 4177 (1995)
H_2 , cat PtO_2	Syn 733 (1981) JOC 58 6804 (1993)
$(\text{NH}_4)_2\text{O}_2\text{CH}$, cat Pd-C	TL 30 317 (1989) JOC 55 4688 (1990); 56 457 (1991); 57 1656 (1992); 58 4993 (1993) SL 153 (1993)
$(\text{NH}_4)_2\text{O}_2\text{CH}$, cat $\text{Pd}(\text{OH})_2\text{-C}$	JOC 57 2114 (1992); 59 649 (1994)
$\left[\text{O} \begin{array}{c} \diagup \quad \diagdown \\ \text{NH}_2 \end{array} \right] \text{O}_2\text{CH}$, cat $\text{Pd}(\text{OH})_2\text{-C}$	JOC 57 2114 (1992)
hv, dioxane ($\text{Ar} = o\text{-NO}_2\text{C}_6\text{H}_4$)	JOC 58 1582 (1993)
hv, 9,10-dicyanoanthracene, H_2O , CH_3CN	TL 29 4157 (1988)

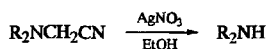
MeLi or LDA	TL 36 1671 (1995)
$\text{ClCO}_2\text{CHClCH}_3/\text{MeOH}$	SL 195 (1993)
AlCl_3	SL 333 (1993)



H_2 , cat Pd-C	JOC 58 4993 (1993)
HCl	JOC 59 653 (1994)
$\text{CF}_3\text{SO}_3\text{H}$	TL 35 2985 (1994)



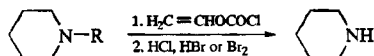
<i>o</i> -HSC ₆ H ₄ CO ₂ H, cat Pd(DBA) ₂ , cat dppb	TL 36 1267 (1995)
<i>N,N'</i> -dimethylbarbituric acid, cat Pd(PPh ₃) ₄	JOC 58 6109 (1993)
KO- <i>t</i> -Bu, DMSO/KMnO ₄	JOC 30 3235 (1965)
cat ClRh(PPh ₃) ₃ , H ₂ O	TL 2591 (1977); 22 1483 (1981) SL 1037 (1995)
cat ClRh(PPh ₃) ₃ , H ₂ O, EtOH	JOC 59 649 (1994)
cat RhCl ₃ , H ₂ O, EtOH	TL 2591 (1977)
cat RhH(PPh ₃) ₄ , CF ₃ CO ₂ H, EtOH	JOC 53 976 (1988)
ClCO ₂ Et/hydrolysis	TL 24 3233 (1983)
ClCO ₂ CH ₂ CCl ₃ /hydrolysis or Zn	TL 1325 (1974); 24 3233 (1983)
Cp ₂ ZrCl ₂ , <i>n</i> -BuLi	JOC 58 774 (1993)



JOC 58 4662 (1993)

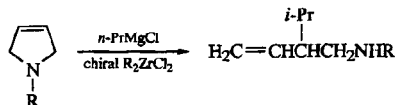


JOC 17 1043 (1952)



TL 1567 (1977)

SL 731 (1990)

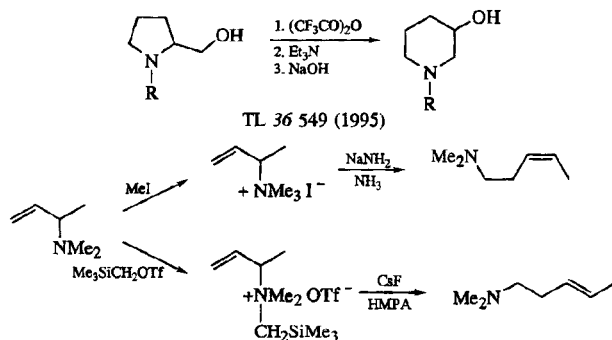


JACS 117 7097 (1995)

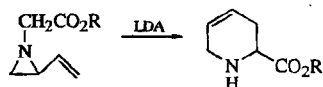
$(R_3\overset{+}{N}R')X^- \longrightarrow R_3N$			
Reagent(s)	R'	X	
Δ	Me, benzylic, allylic	halide	Org Rxs 7 142 (1953) (review)
	Me	OAc	Tetr 24 5493 (1968)
	alkyl	OH	Org Rxs 11 317 (1960) (review)
$LiAlH_4$	Me	I	JACS 82 4651 (1960)
	Me, Et	I	JCS 1729 (1965)
LiI	Me	OTs	JOC 28 2407 (1963)
KO_2CH, HCO_2H	Me	Br	Coll Czech Chem Commun 26 471 (1961)
$KOAc$	Me	Br	Coll Czech Chem Commun 26 471 (1961)
$NaSPh$	Me	Cl	TL 1375 (1966)
	Me, Et	I	JCS 1729 (1965)
$H_2NCH_2CH_2OH$	various alkyl	halide, ClO_4	Ber 90 395, 403 (1957)

6. Rearrangement

For *N*-Cope rearrangements, see Syn 71 (1989) (review).

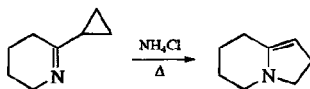


JACS 112 1999 (1990) (stereospecific for trisubstituted double bonds also)

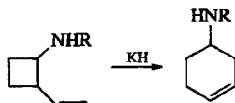


JACS 116 9781 (1994)

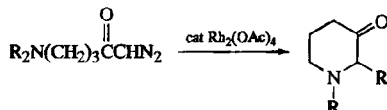
TL 36 303, 3557 (1995)



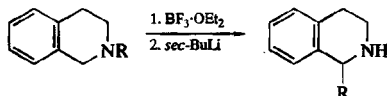
TL 3799 (1976); 837 (1979); 23 1413 (1982); 24 3409 (1983); 31 5441 (1990)
 Acct Chem Res 10 193 (1977)
 JACS 107 2192 (1985); 110 8250 (1988)



JACS 110 8111 (1988)

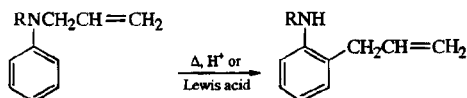


JACS 115 1177 (1993); 116 8420 (1994)

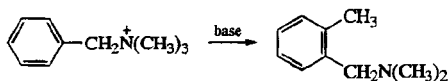


R = allylic, benzylic

TL 36 8481 (1995)



JOC 22 1418 (1957); 58 5095 (1993)
 TL 4661 (1971); 25 3159 (1984); 34 6849 (1993) (BF₃·OEt₂)
 Helv 56 105 (1973); 60 978 (1977)
 Yakugaku Zasshi 97 553 (1977)
 JOC USSR 15 2350 (1979); 18 1278 (1982); 19 920 (1983)
 Bull Acad Sci USSR, Div Chem Sci 1910 (1982)
 Chem Pharm Bull 31 2220 (1983)



Sommelet-Hauser rearrangement

JACS 73 4122 (1951); 79 4449 (1957)

Org Syn 34 61 (1954)

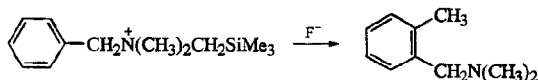
Org Rxns 18 403 (1970) (review)

A. R. Lepley, A. G. Giumanini in "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, Wiley Interscience, New York (1971), Vol 3, p 297 (review)

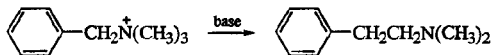
JOC 36 984 (1971); 44 2348 (1979)

I. Zugravescu, M. Petrovanu, "N-Ylid Chemistry," McGraw-Hill, New York (1976), Chpt 2 (review)

J Heterocyclic Chem 18 63 (1981)



JOC 52 1844 (1987); 53 194 (1988); 54 836 (1989); 55 2767 (1990); 57 5034 (1992); 59 7897 (1994); 60 4272 (1995)



Stevens rearrangement

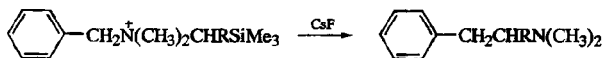
Org Rxns 18 403 (1970) (review)

A. R. Lepley, A. G. Giumanini in "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, Wiley Interscience, New York (1971), Vol 3, p 297 (review)

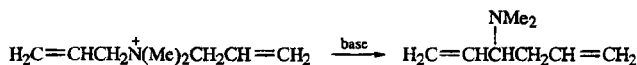
JOC 36 984 (1971); 44 2348 (1979)

I. Zugravescu, M. Petrovanu, "N-Ylid Chemistry," McGraw-Hill, New York (1976), Chpt 2 (review)

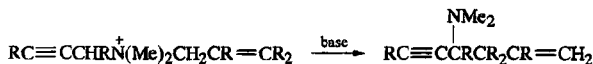
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 3.10, p 913 (review)



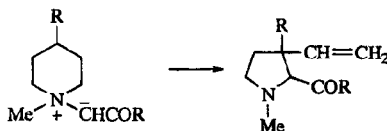
JOC 55 334 (1990); 57 5034 (1992); 60 4272 (1995)



JCS Perkin I 1436 (1980)



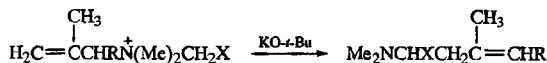
JCS Perkin I 1436 (1980)



CC 656 (1973)

JCS Perkin I 1953 (1981)

TL 29 3993 (1988); 31 4351 (1990); 32 2827 (1991)

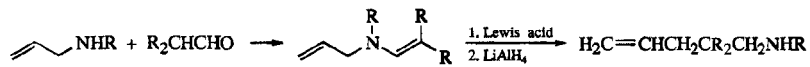


X = COR, CO₂R, CH=CHCO₂R

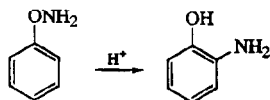
JOC 57 428 (1992)



CC 1493 (1971); 657 (1973)



JOC 57 461, 7188 (1992)

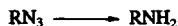


JACS 114 9795 (1992)

6. FROM AZIDES

Review: Chem Rev 88 297 (1988)

See also page 761, Section 3, and page 835, Section 2.



H ₂ , Raney Ni	JACS 111 1063 (1989)
H ₂ , cat Pd or Pt	Chem Rev 54 1 (1954) (review)
H ₂ , cat Pd-C	J Med Chem 12 658 (1969) CC 915 (1970); 1738 (1987) JOC 36 250 (1971); 37 335 (1972); 50 3095 (1985); 51 1069, 5373 (1986); 54 3292 (1989); 58 3736 (1993); 59 813, 2179, 6419 (1994); 60 8318 (1995) Ber 105 1524 (1972) TL 28 4601 (1987); 29 1279 (1988); 30 837 (1989); 32 7175 (1991); 36 3465 (1995) JACS 112 4011 (1990)
H ₂ , cat Pd-Al ₂ O ₃	JOC 56 3125 (1991)
H ₂ , cat Pd-CaCO ₃	Syn 590 (1975)
H ₂ , cat Pd(OH) ₂ -C	JOC 56 3043 (1991); 59 6804 (1994)
H ₂ , cat PdO	JACS 76 2887 (1954)
H ₂ , cat PtO ₂	JOC 27 3045 (1962); 40 1659 (1975); 54 1866, 3292 (1989); 60 4884 (1995) TL 28 4499 (1987)
HCO ₂ H, cat Pd-C	JOC 58 1762 (1993)
(NH ₄)O ₂ CH, cat Pd-C	TL 24 1609 (1983); 28 6133 (1987); 36 8247 (1995) JOC 57 5692 (1992)
N ₂ H ₄ , cat Pd(OH) ₂ -C	Syn 450 (1989) JOC 56 3043 (1991); 59 6804 (1994)

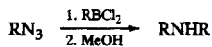


BH_3	JACS 87 4203 (1965); 89 2077 (1967)
$\text{HBCl}_2 \cdot \text{SMe}_2$	TL 36 7987 (1995)
$\text{LiBH}_3\text{NMe}_2$	JOC 59 6378 (1994) TL 36 2567 (1995)
NaBH_4 , H_2O , (dioxane)	JOC 23 127 (1958)
NaBH_4 , MeOH , THF	Syn 48 (1987)
NaBH_4 , $i\text{-PrOH}$, Δ	JACS 84 485 (1962); 86 1427 (1964) Chem Pharm Bull 18 2368 (1970)
NaBH_4 (phase transfer)	JOC 47 4327 (1982)
NaBH_4 -exchange resin	Syn Commun 20 293 (1990)
NaBH_4 , cat CoBr_2	JOC 60 4324 (1995)
NaBH_4 -exchange resin, $\text{Ni}(\text{OAc})_2$, MeOH	Syn Commun 23 3047 (1993)
NaBH_4 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	Chem Ind 764 (1987)
$\text{Zn}(\text{BH}_4)_2$	JOC 59 4114 (1994)
LiAlH_4	JACS 73 5865 (1951); 91 2961 (1969); 92 6302 (1970); 108 2034 (1986); 110 6467 (1988) Chem Rev 54 1 (1954) (review) JOC 27 2925 (1962); 31 684 (1966); 51 5373 (1986); 60 2570 (1995) Carbohydr Res 3 318 (1967) CL 635 (1977) TL 32 4321 (1991) SL 337 (1991) Tetr Asym 5 1727 (1994)
$n\text{-Bu}_3\text{SnH}$	JACS 107 519 (1985) TL 28 6381 (1987); 32 6293 (1991) SL 342 (1991)
$n\text{-Bu}_2\text{SnH}_2$	TL 28 5941 (1987)
Mg , MeOH	Syn Commun 18 1201 (1988)
Ca , MeOH	Syn Commun 18 1201 (1988)
Raney Ni	Syn 24 (1978) Org Syn Coll Vol 7 433 (1990)
Zn , HCl	CC 64 (1970) JCS C 414 (1971) JOC 54 3292 (1989)
Zn , HOAc	JCS C 414 (1971)
SnCl_2 , MeOH	TL 27 1423 (1986); 28 4597 (1987) JACS 111 8912 (1989); 116 8544 (1994)
TiCl_3 , H_2O	Syn 65 (1978)
VCl_2 , H_2O ($\text{R} = \text{aryl}$ only)	Syn 815 (1976)

CrCl ₂ , H ₂ O	CC 64 (1970) JCS C 414 (1971) Tetr 29 1801 (1973)
MoCl ₅ , Zn, H ₂ O, THF	Syn 830 (1980)
SmI ₂	TL 36 7313, 7427 (1995)
H ₂ S, solvent?	Chimia 22 141 (1968)
H ₂ S, H ₂ O	JACS 73 2327 (1951)
H ₂ S, H ₂ O, py	Syn 45 (1977) JOC 59 7944 (1994)
H ₂ S, H ₂ O, py, Et ₃ N	SL 57 (1993)
H ₂ S, EtOH	JOC 33 2910 (1968) Tetr 23 387 (1967); 25 3313 (1969) Monatsh 101 724 (1970)
HS(CH ₂) ₃ SH, Et ₃ N	TL 3633 (1978) JACS 110 7910 (1988); 116 487 (1994) JOC 56 4326 (1991)
PhSH, Sn(SPh) ₂ , Et ₃ N	TL 28 5941 (1987)
Na ₂ S·9H ₂ O, Et ₃ N, MeOH	JOC 44 4712 (1979)
(NH ₄) ₂ S, EtOH, H ₂ O	JACS 113 8419 (1991)
(Me ₃ Si) ₂ S, MeOH	JOC 60 2254 (1995)
(PhCH ₂ NEt ₃) ₂ MoS ₄ (R = Ar)	JOC 60 7682 (1995)
NaTeH	CL 1733 (1984)
P(OEt) ₃ / TsOH, EtOH	TL 28 6513 (1987)
P(OEt) ₃ / HCl	Syn 202 (1985)
Me ₃ P / H ₂ O	JOC 59 4800 (1994)
PPh ₃ , H ₂ O	TL 24 763 (1983); 28 379, 1757, 1761 (1987) BSCF 815 (1985) JOC 52 5044 (1987); 57 441 (1992); 59 4450 (1994) JACS 110 7910 (1988); 115 12550 (1993); 116 487, 8544 (1994) SL 63 (1992)
PPh ₃ / HCl or HBr	Ann 591 117 (1955) TL 32 7175 (1991)
PPh ₃ / NH ₄ OH or NaOH	JOC 40 1659 (1975); 54 3292 (1989); 60 4786 (1995) TL 27 227 (1986)
CH ₃ COCH ₂ COCH ₃ , Et ₃ N	J Heterocyclic Chem 10 565 (1973) JOC 40 1066 (1975) Syn 491 (1977) TL 28 5941 (1987)



JOC 42 2935 (1977)



See page 761, Section 3.

X = halogen, O₃SR; n = 2, 4, 5H₂, cat Pd-C

TL 31 3637 (1990)

JOC 56 1386 (1991); 57 5178 (1992)

H₂, cat Pd-BaSO₄

JOC 56 1386 (1991)

LiAlH₄

JACS 91 5046 (1969)

Angew Int 13 279 (1974)

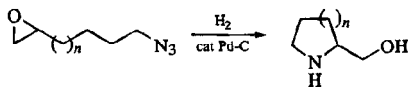
TL 35 2039 (1994)

(Me₃Si)₃SiH, AIBN

JACS 116 5521 (1994)

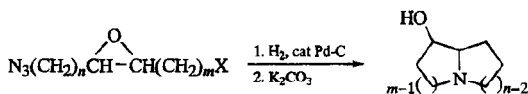
n-Bu₃SnH, AIBN

JACS 116 5521 (1994)



n = 1, 2

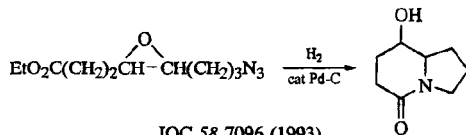
TL 30 7261 (1989); 32 5517 (1991)



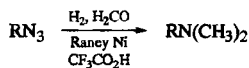
n = 3, 4; m = 2, 3; X = Cl, OTs

TL 32 5513 (1991); 34 8221 (1993)

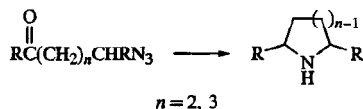
JOC 56 1976 (1991); 57 3977 (1992)



JOC 58 7096 (1993)



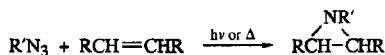
TL 32 7175 (1991)

H₂, cat Pd-C

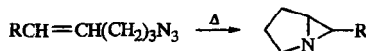
Angew Int 27 716 (1988)
 TL 29 4645 (1988); 35 359 (1994)
 Heterocycles 28 477 (1989)
 JACS 111 3924 (1989); 113 6187, 6678 (1991)
 JOC 56 6280 (1991); 58 4809 (1993)
 SL 999 (1992)

H₂, cat PtO₂-C

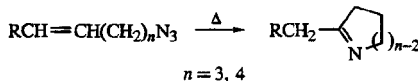
JOC 55 3926 (1990)



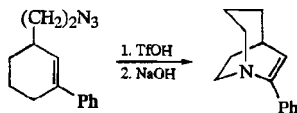
JOC 30 7 (1965); 39 3739 (1974); 54 3945 (1989) [R' = C(OR)=NMs or C(OR)=NCN]; 55 2034, 2103
 (intramolecular) (1990)
 TL 29 3525, 3695 (1988)
 JACS 115 10742, 12305 (1993)



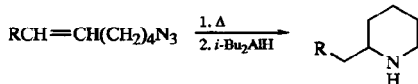
JOC 53 2094 (1988); 55 4683 (1990)



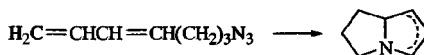
JOC 53 2968 (1988)
 JACS 111 2580 (1989)
 TL 31 5437, 5441, 7571 (1990); 32 6469 (1991)



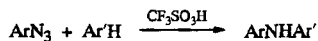
JACS 115 10183 (1993)



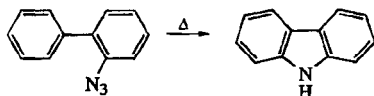
JOC 60 529 (1995)



. SL 433 (1990) (review)



JOC 58 6900 (1993)



TL 30 297 (1989)



JOC 43 4271 (1978); 58 7848 (1993); 59 4875, 7962 (1994); 60 790, 2368 (1995)

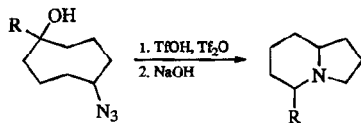
TL 27 4157 (1986); 30 4881 (1989); 36 3639 (1995)

Heterocycles 25 541 (1987)

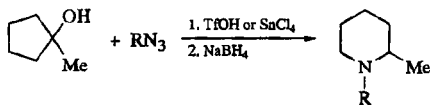
Rec Trav Chim III 1 (1992)

SL 527 (1992); 64 (1995)

Tetr Asym 5 1727 (1994)



JACS 115 10183 (1993)



JOC 60 4960 (1995)

7. FROM NITRO COMPOUNDS

Reviews:

- R. L. Augustine, "Catalytic Hydrogenation," Marcel Dekker, New York (1965), Chpt 5
 M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 10
 M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary,"
 J. Wiley & Sons, New York (1978), Chpt 5
 P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 8
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
 Vol 8, Part 2.1, p 363



R = alkyl

H ₂ , Raney Ni	Ber 86 939 (1953) JOC 53 5552 (1988); 59 5078 (1994) TL 30 731 (1989)
H ₂ , Raney Ni, HOAc	Org Syn Coll Vol 4 221 (1963)
H ₂ , cat Pd-C	Ber 86 939 (1953) JACS 81 505 (1959) CL 797 (1981) TL 30 731 (1989) JOC 58 2302 (1993)
H ₂ , cat Pd(OH) ₂ -C	TL 32 1711 (1991)
H ₂ , cat PtO ₂	JOC 37 335 (1972) SL 531 (1992)
H ₂ , cat RhCl ₃ (py) ₃ ·NaBH ₄	JCS Perkin I 2509 (1973)
H ₂ , cat RuCl ₂ (PPh ₃) ₃ , KOH	JOC 40 519 (1975)
LiBH ₄ , MeOH, diglyme	JOC 51 4000 (1986)
NaBH ₄ , CoCl ₂ ·6H ₂ O	TL 4555 (1969) CC 344 (1986)
NaBH ₄ , cat NiCl ₂ ·6H ₂ O	TL 26 6413 (1985) JOC 51 4856 (1986)

NaBH ₄ , cat Pd-C	Syn 713 (1987)
NaBH ₄ , cat CuSO ₄	SL 419 (1990)
borohydride exchange resin, cat Ni(OAc) ₂	SL 135 (1993)
LiAlH ₄	JACS 70 3738 (1948); 73 1293 (1951); 112 323 (1990); 114 5959 (1992) TL 28 6281 (1987) JOC 55 4474 (1990)
NaAlH ₄	JOC 58 4727 (1993)
Mg(Hg)-TiCl ₄ , <i>t</i> -BuOH, THF	Syn Commun 13 495 (1983)
Al(Hg), H ₂ O	JACS 90 3245 (1968) TL 28 6281 (1987)
Al(Hg), H ₂ O, sonication	TL 35 3187, 6013 (1994)
Sn, HCl	Org Syn Coll Vol 2 617 (1943)
Zn, HCl	TL 28 577 (1987)
Fe, HCl	JACS 73 1293 (1951)
FeSO ₄ , KHCO ₃ /NaBH ₄ /CO ₂ , H ₂ O	Tetr 47 6113 (1991)
FeSO ₄ ·7H ₂ O, NiSO ₄ ·6H ₂ O, KHCO ₃ /NaBH ₄ /CO ₂ , H ₂ O	JOC 60 1201 (1995)
SmI ₂ , MeOH, THF	TL 32 1699 (1991); 34 4743 (1993)
(NH ₄) ₂ O ₂ CH, cat Pd-C	TL 25 3415 (1984) JOC 51 4856 (1986) Syn Commun 20 459 (1990) JACS 114 10181 (1992)
HCO ₂ H, CF ₃ CO ₂ H, cat Pd-C	TL 35 6255 (1994)
H ₃ PO ₂ , cat Pd-C	TL 35 6255 (1994)
cat Pd, cyclohexene	JCS 3586 (1954)
CO, Ru ₃ (CO) ₁₂ , NaOH (phase transfer)	TL 21 2603 (1980)
N ₂ H ₄ ·2H ₂ O, Ni ₂ B	JOC 51 4294 (1986)



JOC 57 778 (1992)



LiBH ₄ , Me ₃ SiCl	Angew Int 28 218 (1989)
NaBH ₄ , EtOH	JCS Perkin I 1373 (1986) JOC 53 2144 (1988)
LiAlH ₄	JOC 55 4474 (1990); 59 5955 (1994)



Review: *Org Rxs* 20 455 (1973) (sulfides and polysulfides)

H ₂ , cat Fe(CO) ₃ (PPh ₃) ₂	<i>JOC</i> 41 1200 (1976)
H ₂ , cat Fe(CO) ₃ (AsPh ₃) ₂	<i>JOC</i> 41 1200 (1976)
H ₂ , cat Ru	<i>JOC</i> 44 1233 (1979)
H ₂ , cat RuCl ₂ (PPh ₃) ₃	TL 2163 (1975) <i>JOC</i> 41 1200 (1976)
H ₂ , cat [RuCl ₂ (CO) ₃] ₂	<i>JOC</i> 41 1200 (1976)
H ₂ , cat RuCl ₂ (CO) ₂ (PPh ₃) ₂	<i>JOC</i> 41 1200 (1976)
H ₂ , cat CoS _x , <i>i</i> -PrOH	<i>JOC</i> 44 3671 (1979)
H ₂ , cat RhCl ₃ (py) ₃ -NaBH ₄	<i>JCS Perkin I</i> 2509 (1973)
H ₂ , cat Ni	<i>JACS</i> 61 3564 (1939)
H ₂ , cat Raney Ni	<i>JOC</i> 18 1506 (1953); 51 3903 (1986); 60 1939 (1995) <i>JACS</i> 76 5149 (1954) <i>Acta Chem Scand</i> 9 1079 (1955) <i>Org Syn Coll Vol</i> 3 59, 63 (1955); 4 357 (1963); 5 1130 (1973)
H ₂ , cat KBH ₄ -NiCl ₂ ·6H ₂ O-C	<i>Carbohydr Res</i> 88 323 (1981)
H ₂ , cat NaBH ₄ -exchange resin-PdCl ₂	<i>Bull Korean Chem Soc</i> 14 281 (1993)
H ₂ , cat Pd-C	<i>JOC</i> 37 335 (1972); 51 3308 (1986); 52 1844, 5717 (1987); 58 6692 (1993) <i>Org Syn Coll Vol</i> 5 829 (1973) <i>Syn</i> 940 (1982) <i>JACS</i> 107 3328 (1985)
H ₂ , cat Pd-CaCO ₃ , PbO, quinoline	<i>JOC</i> 58 471 (1993)
H ₂ , cat Pd(acac) ₂ , py	<i>Chem Ind</i> 1057 (1975)
H ₂ , cat Pd(hfacac) ₂ -M ₂ Si(OSiHMe) _n OSiMe ₃	TL 34 3075 (1993)
H ₂ , cat montmorillonite-Pd	TL 30 251 (1989)
H ₂ , cat PtO ₂	<i>Org Syn Coll Vol</i> 1 240 (1941)
H ₂ , cat PtO ₂ , K ₂ CO ₃ , CH ₃ OH	<i>JOC</i> 44 409 (1979)
H ₂ , cat Pt salt-NaBH ₄	<i>JACS</i> 84 2828 (1962)
cat Pd, cyclohexene	<i>JCS</i> 3586 (1954)
cat Pd-C, cyclohexene	<i>JCS Perkin I</i> 1300 (1975) <i>JOC</i> 59 754 (1994)
N ₂ H ₄ , (catalysts)	<i>Chem Rev</i> 65 51 (1965) (review)
N ₂ H ₄ , montmorillonite (K-10)	TL 31 1181 (1990)
N ₂ H ₄ , graphite	TL 26 6233 (1985)

N_2H_4 , $FeCl_3 \cdot 6H_2O$, C, CH_3OH	CL 259 (1975) JOC 50 5092 (1985); 52 1339 (1987); 59 192 (1994) JACS 112 9364 (1990)
N_2H_4 , Fe(III) oxide	Syn 834 (1978)
N_2H_4 , Raney Ni	JACS 75 4334 (1953); 76 5149 (1954) J Gen Chem USSR 27 261 (1957) Can J Chem 38 2363 (1960) TL 23 147 (1982) BCSJ 56 3159 (1983)
N_2H_4 , cat Pd-C	Org Syn Coll Vol 5 30 (1973) JCS Perkin I 444 (1977)
Me_2NNH_2 , cat $FeCl_3 \cdot 6H_2O$	TL 36 2411 (1995)
$PhNHNH_2$	JCS 330 (1929)
HCO_2H , cat Pd-C	JCS Perkin I 443 (1977) TL 35 6255 (1994)
HCO_2H , CF_3CO_2H , cat Pd-C	TL 35 6255 (1994)
NaO_2CH , KH_2PO_4 , <i>N</i> -methylpyrrolidone	Syn Commun 11 925 (1981)
KO_2CH , cat Pd-C	JOC 56 4481 (1991)
$(NH_4)O_2CH$, cat Pd-C	TL 25 3415 (1984); 29 5733 (1988) Syn 133 (1986)
$(Et_3NH)O_2CH$, cat $RuCl_2(PPh_3)_3$, cat Pd-C	JOMC 309 C63 (1986)
$(Et_3NH)O_2CH$, cat $Pd(OAc)_2(PAr_3)_2$	JOC 42 3491 (1977)
$(Et_3NH)O_2CH$, cat Pd-C	JOC 42 3491 (1977); 45 4992 (1980) JACS 108 1000 (1986)
H_3PO_2 , cat Pd-C	TL 35 6255 (1994)
phosphinic acid or sodium phosphinate or phosphorous acid or sodium phosphite, cat Pd-C	JCS Perkin I 443 (1977)
$(Et_3NH)H_2PO_2 \cdot 1.5H_2O$, Raney Ni	JOC 54 949 (1989)
CO, H_2O , Se, Et_3N	Angew Int 19 1008 (1980)
CO, $Ru_3(CO)_{12}$, NaOH (phase transfer)	TL 21 2603 (1980)
CO, Rh catalyst, H_2O	TL 3385 (1971)
CO, cat $Pd(OAc)_2$, PR_3 , HOAc, H_2O	Bull Acad Sci USSR, Div Chem Sci 1223 (1986)
$Fe(CO)_5$	Can J Chem 48 1543 (1970)
$Fe(CO)_5$, CO, H_2O , Et_3N	JACS 100 3969 (1978)
$Fe_2(CO)_9$, aq NaOH, C_6H_6	JACS 99 98 (1977)
$Fe_3(CO)_{12}$, CH_3OH	JOC 37 930 (1972)
$Fe_3(CO)_{12}$, Al_2O_3	CC 821 (1980)

$\text{Fe}_3(\text{CO})_{12}$, aq NaOH, C_6H_6 , cat $(\text{PhCH}_2\text{NEt}_3)\text{Cl}$	JACS 99 98 (1977)
$\text{Fe}_3(\text{CO})_{12}$, KOH, 18-crown-6	Angew Int 16 41 (1977)
$(\text{Et}_4\text{N})\text{HFe}_3(\text{CO})_{11}$	JOMC 171 85 (1979)
$\text{HFe}(\text{CO})_4^-$, $\text{CF}_3\text{CO}_2\text{H}$	TL 29 5083 (1988)
LiBH_4 , MeOH, diglyme	JOC 51 4000 (1986)
NaBH_2S_3	Can J Chem 49 2990 (1971)
NaBH_4 , cat Pd-C	Syn 713 (1987)
NaBH_4 , cat Pd-C, H_2O	JCS 371 (1962)
NaBH_4 , $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, EtOH	Chem Pharm Bull 29 1443 (1981) JACS 114 980 (1992)
NaBH_4 , TiCl_4	Syn 695 (1980)
NaBH_4 , cat MoO_3 , cat Na_2SeO_3	TL 33 1463 (1992)
NaBH_4 , FeCl_2	Chem Ind 480 (1983)
NaBH_4 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	TL 4555 (1969)
NaBH_4 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	Chem Pharm Bull 29 1159 (1981) JOC 60 4006 (1995)
NaBH_4 , $\text{NiX}_2(\text{PPh}_3)_2$ (X = Cl, Br, I)	JCS Japan 92 1225 (1971)
NaBH_4 , CuCl	Chem Ind 75 (1984)
NaBH_4 , $\text{Cu}(\text{OAc})_2$	TL 27 1205 (1986) SL 791 (1993)
NaBH_4 , cat $\text{Cu}(\text{acac})_2$	JCS Perkin I 2409 (1979)
NaBH_4 , cat CuSO_4	SL 419 (1990)
KBH_4 , cat PdCl_2	BSCF 1996 (1959)
KBH_4 , Cu_2Cl_2	Syn Commun 19 3047 (1989)
borohydride exchange resin, cat $\text{Ni}(\text{OAc})_2$	SL 135 (1993)
LaNi_5H_6	JOC 52 5695 (1987)
$\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_5$	JOC 52 5695 (1987)
Li, NH_3 , CH_3OH	Syn Commun 12 293 (1982)
Na, NH_3 , CH_3OH	JACS 69 1657 (1947) Syn Commun 12 293 (1982) JOC 51 3904 (1986)
$\text{Na}(\text{Hg})$, CH_3OH	JOC 60 1070 (1995)
$\text{Mg}(\text{Hg})\text{--TiCl}_4$, <i>t</i> -BuOH, THF	Syn Commun 13 495 (1983)
$(\text{Ni})_2\text{B}$, MeOH, HCl	TL 34 3083 (1993)
Al, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	TL 31 4065 (1990)
Al_2Te_3 , H_2O	Angew Int 19 1009 (1980)

Sn, HCl	JACS 61 1001 (1939); 91 3544 (1969); 109 3098 (1987) Org Syn Coll Vol 1 455 (1941); 2 175 (1943) JCS 1133 (1949)
SnCl ₂ ·2H ₂ O, ROH	TL 25 839 (1984); 26 1362 (1985) 3 115 3199 (1993); 116 8784 (1994) 60 4006 (1995)
SnCl ₂ , HCl	Ber 62 3035 (1929) Org Syn Coll Vol 2 130, 254 (1943); 3 239, 453 (1955) Chem Ind 888 (1972)
SnBr ₂ , HBr	Org Syn Coll Vol 2 132 (1943)
TiO ₂ , EtOH, hv	JOC 58 744 (1993)
TiCl ₃ , H ₂ O	Chem Pharm Bull 28 2515 (1980)
CrCl ₂ , CH ₃ OH	Syn 792 (1977)
Fe	JACS 66 1781 (1944) JOMC 65 289 (1974)
Fe, HOAc	Org Syn Coll Vol 2 471 (1943) JOC 56 4706 (1991)
Fe, HCl	Org Syn Coll Vol 2 160 (1943); 5 346 (1973) JOC 60 3365 (1995)
Fe, FeSO ₄ , H ₂ O	JCS 538 (1944) JOC 59 5535 (1994); 60 6389 (1995)
FeSO ₄ , HCl	Org Syn Coll Vol 3 56 (1955)
FeSO ₄ ·7H ₂ O, NH ₄ OH	JOC 60 2912 (1995)
Zn, H ₂ O	Org Syn Coll Vol 2 447 (1943)
Zn, EtOH	JOC 56 3048 (1991)
Zn, HCl	Proc Ind Acad Sci A 44 331 (1956)
Zn, NaOH	Org Syn Coll Vol 2 501 (1943)
Zn, NH ₃	Tetr 5 340 (1959)
Na ₂ S	Org Syn Coll Vol 3 86 (1955) TL 29 635 (1988)
Na ₂ S, S, NaOH	Org Syn Coll Vol 4 31 (1963)
Na ₂ S, S, NH ₄ Cl	JOC 51 3903 (1986)
Na ₂ S, Me ₃ SiCl	JOC 58 4742 (1993)
Na ₂ S ₂	Org Syn Coll Vol 5 1067 (1973)
Na ₂ S ₂ O ₄	Org Syn Coll Vol 3 69 (1955)
Na ₂ S ₂ O ₄ , cat viologen, K ₂ CO ₃	TL 34 7445 (1993)

(NH ₄) ₂ S	Org Syn Coll Vol 1 52 (1941); 3 82, 242 (1955)
Me ₃ SiSNa	JOC 57 5254 (1992)
NaTeH (sterically hindered Ar only)	CL 1373 (1983)
baker's yeast	Heterocycles 31 2201 (1990) (heterocycles) TL 35 7867 (1994)
baker's yeast, NaOH	TL 35 3965 (1994)
rat liver microsomes	JOC 56 2237 (1991)
paraffin, 360–390°C	Syn 23 (1978)
electrolysis	Topics Curr Chem 148 69 (1988) (review)
electrolysis, NaOH	JOC 54 3740 (1989)
electrolysis, H ₂ SO ₄	SL 68 (1994)



H ₂ , cat RuCl ₂ (PPh ₃) ₃	JOC 41 1200 (1976)
H ₂ , cat Rh-Al ₂ O ₃ , cat Fe	TL 31 6141 (1990)
H ₂ , cat Pd	JOC 8 331 (1943)
H ₂ , cat Pd-C	Syn 726 (1974)
H ₂ , cat Pd-C, NH ₄ OH	Ann NY Acad Sci 214 150 (1973)
H ₂ , cat Pd-C, cat Fe	TL 31 6141 (1990)
H ₂ , cat PdCl ₂ , cat Fe	TL 31 6141 (1990)
H ₂ , cat PtO ₂ , cat Fe	TL 31 6141 (1990)
H ₂ , Raney Cu	Ann NY Acad Sci 158 471 (1969)
Ni, HOAc, maleic acid	Chem Ind 826 (1983)
Raney Ni, <i>i</i> -PrOH, HOAc	Chem Ind 477 (1983)
Raney Ni, N ₂ H ₄ , H ₂ O	Chimia 19 462 (1965)
cat Pd, cyclohexene	JCS 3586 (1954)
cat Pd-C, cyclohexene	JCS Perkin I 1300 (1975) JOC 56 4706 (1991)
HCO ₂ H, Et ₃ N, cat Pd-C	JOC 45 4992 (1980)
SnCl ₂ , HCl	Ber 19 2161 (1886) Rec Trav Chim 65 207, 331 (1946)
Fe, HOAc	Syn 924 (1978)
sulfides and polysulfides	Org Rxn 20 455 (1973) (review)
baker's yeast	TL 35 7867 (1994)
baker's yeast, NaOH	TL 35 3965 (1994)

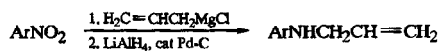


H₂, H₂CO, CH₃OH, Raney Ni

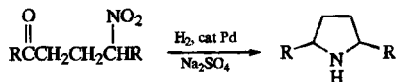
Ind J Chem B 14 904 (1976)

H₂, H₂CO, EtOH, cat Pd-C

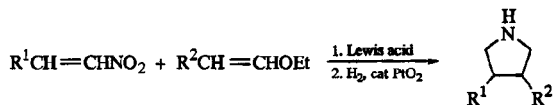
Org Syn Coll Vol 5 552 (1973)



TL 29 2251 (1988)



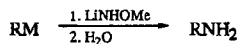
CC 102 (1982)



JOC 58 3857 (1993); 59 4576 (1994); 60 3221 (1995)

8. HETEROATOM AND METAL DISPLACEMENT

See also page 792, Section 3 and page 831, Section 9.



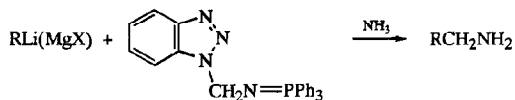
RM = RLi (aryl, alkyl); ArMgX; R₂CuLi (aryl, alkyl)

JOC 54 5574 (1989)



R = 1°, 2°, 3° alkyl; aryl

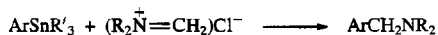
JOC 58 5620 (1993)



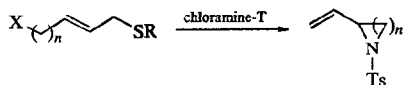
TL 30 3303 (1989)



TL 29 4949 (1988)

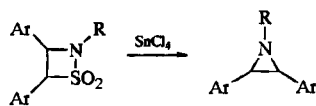


TL 27 5011 (1986)

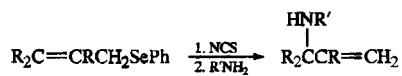


X = halide, OTs, epoxide, 2-alkenoate ester; n = 1-4

TL 30 4723 (1989)



TL 36 5559 (1995)

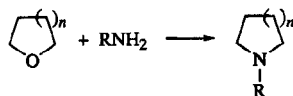


JOC 51 5243 (1986)

9. FROM ETHERS, ALCOHOLS AND DERIVATIVES

See page 779, Section 4, for amination via tosylates and page 815, Section 6, for azide + alcohol \rightarrow amine.

Review: Russ Chem Rev 49 14 (1980)



n

Reagent(s)

0-2

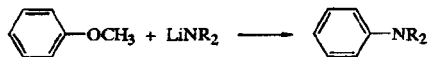
TiO₂

TL 31 2991 (1990)

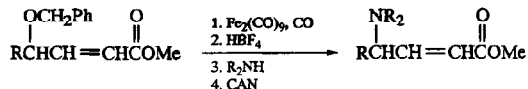
1

zeolite

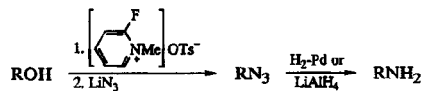
JOC 59 3998 (1994)



JOC 58 5101 (1993)

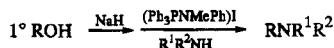


SL 401 (1993)

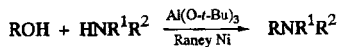


R = 1°, 2° alkyl; allylic; benzylic

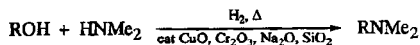
CL 635 (1977)



TL 471 (1975)

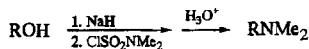


Syn 722 (1977)



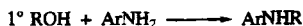
TL 1937 (1977)

Syn Commun 8 27 (1978)



R = allylic, benzylic

JACS 87 5261 (1965)



Raney Ni

JACS 77 4052 (1955)

Org Syn Coll Vol 4 283 (1963)

KOH

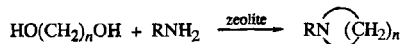
Org Syn Coll Vol 4 91 (1963)



TL 22 2667 (1981)



TL 23 229 (1982)

 $n = 4, 5$

JOC 59 3998 (1994)

 n

2

Reagent(s) $\text{Ph}_3\text{P}(\text{OEt})_2$

Phosphorus 1 151 (1971)

JOC 51 95 (1986)

 Ph_3PCl_2

JACS 99 1272 (1977)

 $\text{Ph}_3\text{P}, \text{CCl}_4, \text{Et}_3\text{N}$

Ber 107 5 (1974)

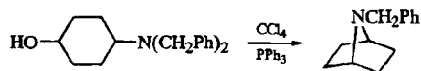
 $\text{Ph}_3\text{PBr}_2, \text{Et}_3\text{N}$

BCSJ 43 1185 (1970)

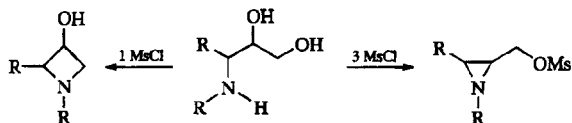
TL 3897 (1974); 31 7579 (1990)

Can J Chem 54 1571 (1976)

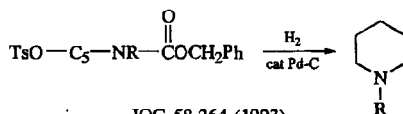
- | | | |
|---|--|--|
| | Ph_3P , $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$ | TL 5153 (1978); 31 7579 (1990)
Syn 969 (1984) |
| | Et_3N , SO_2Cl_2 | TL 33 3013 (1992) |
| | $\text{Et}_3\text{N}\cdot\text{SO}_3$ | Chem Pharm Bull 26 394 (1978) |
| | $\text{TsCl}/\text{Et}_3\text{N}$ | TL 31 7579 (1990)
JOC 58 7848 (1993) |
| 3 | Ph_3P , CCl_4 , Et_3N | Syn 105 (1979) |
| | Ph_3P , CBr_4 | CC 682 (1983) |
| | HX ($\text{X} = \text{Br}$, BF_4)/ Ph_3P ,
$\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$ | CC 682 (1983) |
| | Ph_3PBr_2 , Et_3N | TL 1867 (1973)
Syn 894 (1974) |
| 4 | Ph_3P , $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$ | TL 32 161 (1991) |
| | Ph_3P , CCl_4 , Et_3N | JOC 59 2487 (1994)
Syn 105 (1979)
JOC 57 5990 (1992); 58 3397 (1993);
60 529 (1995) |
| | Ph_3P , CBr_4 , Et_3N | JOC 57 2876 (1992); 59 1358 (1994) |
| | Ph_3PO , TiF_2O | SL 423 (1990) |
| | cat $\text{RuH}_2(\text{PPh}_3)_4$ | TL 23 229 (1982) |
| 5 | Ph_3P , $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$ | TL 32 161 (1991) |
| | Ph_3P , CCl_4 , Et_3N | JOC 60 4177 (1995)
Syn 387 (1980)
JOC 60 5706 (1995) |
| | SOCl_2 | Syn 387 (1980) |
| | alumina | Syn 387 (1980) |
| | cat $\text{RuH}_2(\text{PPh}_3)_4$ | TL 23 229 (1982)
SL 693 (1991) |
| 6 | cat $\text{RuH}_2(\text{PPh}_3)_4$ | TL 23 229 (1982) |



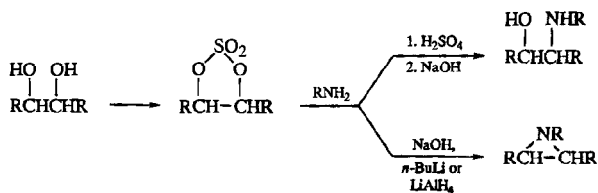
TL 36 1709 (1995)



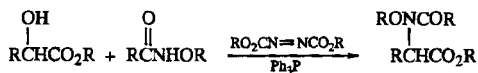
TL 32 6935 (1991)



JOC 58 264 (1993)



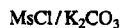
TL 30 2623 (1989)



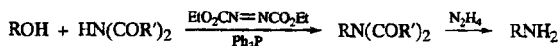
JOC 52 4978 (1987)



JOC 57 5813 (1992)



JOC 59 4875 (1994)

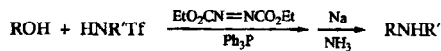


JACS 94 679 (1972)

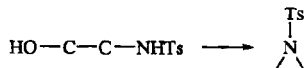
JOC 52 5127 (1987)

Org Syn Coll Vol 7 501 (1990)

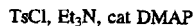
For further alkylations of imides, see page 779, Section 4.



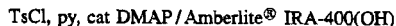
TL 31 3417 (1990)



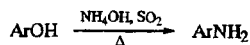
JOC 58 5019 (1993)



SL 41 (1992)



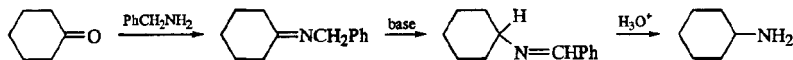
SL 41 (1992)



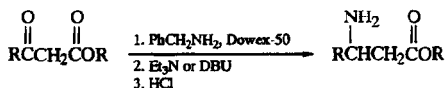
JOC 25 214 (1960)

10. FROM ALDEHYDES, KETONES AND DERIVATIVES

1. Transamination



Can J Chem 48 570 (1970)
 TL 35 3119 (1994); 36 3917 (1995) (chiral)

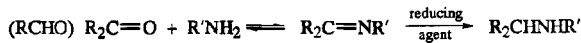


TL 34 3621 (1993)

2. Reductive Amination

Review: Org Prep Proc Int 26 193 (1994) (asymmetric reduction of C=N)

See also page 1097, Section 2.16.



Reviews and key references:

Org Rxs 4 174 (1948)

M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 16

M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J.

Wiley & Sons, New York (1978), Chpt 10

Russ Chem Rev 49 14 (1980)

JOC 48 3412 (1983) (stereoselectivity of various metal hydride reagents)


TL 30 1081 (1989) (stereoselectivity of various metal hydride reagents)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),

Vol 8, Part 1.2, p 25

"Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 1 (hydrogenation)
 Org Prep Proc Int 26 193 (1994)
 Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21d, G. Thieme, Stuttgart-New York
 (1995), p 4199 (enantioselective)

Reducing agent

H ₂ , cat chiral titanocene (enantioselective)	JACS 114 7562 (1992); 116 8952, 9373, 11703 (1994)
H ₂ , chiral Cp ₂ Ti(BINAP)- <i>n</i> -BuLi-PhSiH ₃	JOC 58 7627 (1993)
H ₂ , cat Ir-chiral bisphosphine (enantioselective)	SL 748 (1995)
H ₂ , cat [Ir(diphosphine)H] ₂ (enantioselective)	JACS 112 9400 (1990)
H ₂ , Raney nickel	JOC 19 1054 (1954); 53 836 (1988) J Chem Res (S) 164 (1981) TL 30 317 (1989); 33 4307 (1992)
H ₂ , cat Pd-C	Angew Int 20 805 (1981) JOC 51 3635 (1986); 55 3767 (1990); 59 2487 (1994) TL 30 2801 (1989); 34 2259 (1993)
H ₂ , cat Pt-C	JOC 31 3875 (1966)
H ₂ , cat PtO ₂	BCSJ 47 2081 (1974) TL 33 4307 (1992)
<i>t</i> -PrOH, Na ₂ CO ₃ , cat ClRh(PPh ₃) ₃	Syn 442 (1981)
HCO ₂ H	Org Rxn 5 301 (1949)
Zn, acid	JACS 62 2159 (1940); 63 972, 2843 (1941)
BH ₃	JOC 30 2877 (1965); 57 6071 (1992) BSCF 4439 (1970)
BH ₃ ·py, MeOH, molecular sieves	JOC 60 5995 (1995)
BH ₃ ·py, HOAc	JCS Perkin I 717 (1984)
BH ₃ ·Me ₂ NH	JOC 26 1437 (1961)
BH ₃ ·Me ₂ NH, HOAc	JOC 48 3412 (1983)
BH ₃ · <i>t</i> -BuNH ₂	TL 22 3447 (1981)
BH ₃ · <i>t</i> -BuNH ₂ , HOAc	JOC 48 3412 (1983) TL 25 695 (1984)
BH ₃ , cat <i>t</i> -BuMe ₂ SiOCH(Me)CH(NH ₂)CPh ₂ OH (enantioselective)	TL 36 8607 (1995)
BH ₃ , cat PhSO(=NH)CH ₂ CPh ₂ OH (enantioselective)	SL 655 (1994)
CB, cat  (enantioselective)	SL 753 (1995)

- (CF₃CO₂)₂BH
NaBH₄
JOC 46 355 (1981)
JOC 22 1068 (1957); 28 3259 (1963); 48 3412 (1983); 51 486 (1986); 53 1708 (1988); 57 4470 (1992); 59 4194, 6973 (1994); 60 4177, 4638 (1995)
Chem Pharm Bull 17 98 (1969)
JACS 107 7524 (1985); 113 1394 (1991); 114 8008 (1992)
TL 28 749 (1987); 30 1081, 4539 (1989); 33 4307 (1992); 35 3411 (1994)
SL 81 (1994); 142 (1995)
- NaBH₄, HOAc
JACS 96 7812 (1974)
Org Prep Proc Int 17 317 (1985) (review)
- NaBH₄-exchange resin, (Et₃NH)Cl
Syn Commun 23 1595 (1993)
- NaBH₄-H₃BO₃
TL 30 1081 (1989)
- NaBH₄-silica
TL 30 1081 (1989)
- NaBH₄; TiCl₄, NiCl₂ or PdCl₂
TL 30 1081 (1989)
- NaBH₄, Ti(O-*i*-Pr)₄
SL 1079 (1995)
- KBH₄
TL 33 4307 (1992)
- NaBH₃OAc
TL 30 1081 (1989)
- NaBH(OAc)₃
TL 30 1081 (1989); 31 5595 (1991)
SL 537 (1990); 81 (1994)
- NaHB(O₂CCHR¹NR²COR³)₃ (enantioselective)
TL 22 3869 (1981)
- LiBH₃NR₂ (R = Et, *i*-Pr)
TL 35 5389 (1994)
- NaBH₃CN
JACS 91 3996 (1969); 93 2897 (1971); 108 1039 (1986); 109 1814 (1987); 111 3436 (1989); 112 4897 (1990)
Syn 135 (1975) (review)
CC 1088 (1979)
Org Prep Proc Int 11 201 (1979) (review)
TL 21 789 (1980); 22 3447 (1981); 30 1081, 3065 (1989); 31 3393 (1990) (intramolecular); 33 4307 (1992); 35 1181 (1994); 36 5081 (1995)
JOC 48 3412 (1983); 52 5044 (1987); 53 5607 (1988); 55 6291 (1990); 57 752, 3854 (1992); 58 3736 (1993); 59 5841 (intramolecular), 6973 (1994)
Org Syn Coll Vol 6 499 (1988)
- NaBH₃CN, HOAc
Org Prep Proc Int 17 317 (1985) (review)
TL 34 6205 (1993) (intramolecular)
- NaBH₃CN, HCl
TL 23 1929 (1982); 30 1081 (1989)
- NaBH₃CN, Ti(O-*i*-Pr)₄
JOC 55 2552 (1990)
- NaBH₃CN, ZnCl₂
JOC 50 1927 (1985); 60 6953 (1995)
- (*n*-Bu₄N)BH₃CN
JOC 46 3571 (1981)

Reducing agent

NaHBR ₂ CN	TL 22 3447 (1981)
LiHBEt ₃	TL 22 3447 (1981); 25 695 (1984)
LiHB(sec-Bu) ₃	TL 22 3447 (1981); 25 695 (1984) JOC 48 3412 (1983)
<i>i</i> -Bu ₂ AlH	TL 23 1929 (1982); 30 1081 (1989) JOC 57 5065 (1992)
<i>i</i> -Bu ₂ AlH, <i>n</i> -BuLi	TL 23 1929 (1982)
<i>i</i> -Bu ₂ AlH, Ti(O- <i>i</i> -Pr) ₄	TL 30 1081 (1989)
<i>i</i> -Bu ₂ AlH, ZnCl ₂	TL 33 5637 (1992) (α -sulfoxide)
LiAlH ₄	Org Rxs 6 469 (1951) (review) JOC 23 535 (1958) BSCF 4439 (1970) TL 23 1929 (1982); 30 1081 (1989)
LiAlH ₄ , LiCl	TL 23 1929 (1982)
LiAlH ₄ , NaOMe	TL 23 1929 (1982)
LiAlH ₄ , BF ₃ ·OEt ₂	TL 23 1929 (1982)
LiAlH ₄ , Me ₃ Al	TL 23 1929 (1982); 30 1081 (1989)
LiAlH ₄ , <i>i</i> -Bu ₃ Al	TL 23 1929 (1982)
LiAlH ₄ , TiCl ₃	TL 23 1929 (1982)
LiAlH ₄ , TiCl ₄	TL 23 1929 (1982); 30 1081 (1989) JOC 58 2867 (1993)
LiAlH ₄ , Ti(O- <i>i</i> -Pr) ₄	TL 23 1929 (1982); 30 1081 (1989)
LiAlH ₄ , NiCl ₂	TL 23 1929 (1982)
LiAlH ₄ , Ni(acac) ₂	TL 30 1081 (1989)
Mg(AlH ₄) ₂	TL 23 1929 (1982)
NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂	JOC 48 3412 (1983)
Et ₃ SiH, CF ₃ CO ₂ H	Bull Acad Sci USSR, Div Chem Sci 1345 (1968)
PhMe ₂ SiH, CF ₃ CO ₂ H	JOC 53 5415 (1988)
<i>n</i> -Bu ₂ SnClH, HMPA	JOC 60 2677 (1995)
MFe(CO) ₄ H (M = Na, K)	Syn 733 (1974) CL 699 (1975) BCSJ 49 1378, 2302 (1976) Tetr 42 259 (1986)
LaNi ₅ H ₆	JOC 52 5695 (1987)
LaNi _{4.5} Al _{0.5} H ₅	JOC 52 5695 (1987)
Na ₂ S ₂ O ₄ , H ₂ O	Austral J Chem 32 201 (1979)

cat o -HSC₆H₄NH₂ or $(o$ -H₂NC₆H₄S)₂, HBr,
ROH

SL 668 (1991)

PhSeH

TL 21 3385 (1980)

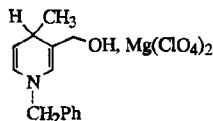
NaTeH

BCSJ 57 3359 (1984)

TL 26 3693 (1985); 29 2571 (1988)

C₈K

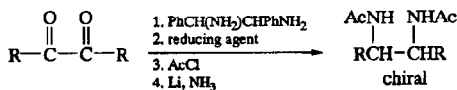
Syn 30 (1979)



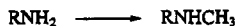
TL 29 5617 (1988)

(NH₄)O₂CH, dithiothreitol, formate dehydrogenase,
amino acid dehydrogenase, NADH (enantioselective,
 α -keto acid)

TL 35 6533 (1994)



JOC 57 6653 (1992)



H₂CO, MFe(CO)₄H (M = Na, K)

Syn 733 (1974)

BCSJ 49 1378 (1976)

H₂CO, succinimide / NaBH₄

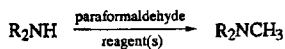
JOC 38 1348 (1973)

H₂CO, 5,5-dimethylhydantoin / NaBH₄

Heterocycles 5 203 (1976)

H₂CO, p -CH₃C₆H₄SH / NaBH₄

Bioorg Chem 8 339 (1979)



Reagent(s)

NaBH₄

TL 261 (1973)

NaBH₄, CF₃CO₂H

Syn 709 (1987)

NaBH₄, H₂SO₄

Syn 743 (1980)

NaBH₄, Ti(O-*i*-Pr)₄

TL 35 2401 (1994)

NaBH₃CN, CH₃CN

JOC 37 1673 (1972)

NaBH₃CN, ZnCl₂, MeOH

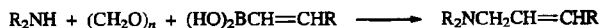
JOC 50 1927 (1985)

KFe(CO)₄H, CO

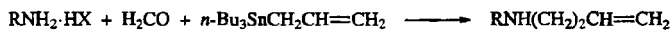
BCSJ 49 1378 (1976)

NaH₂PO₃

TL 25 2535 (1984)



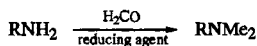
TL 34 583 (1993)



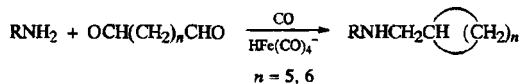
JOC 52 1378 (1987)



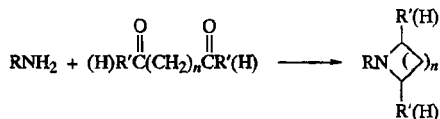
JOC 60 4928 (1995)

Reducing agent

H_2 , cat Pd-C	JOC 59 4297 (1994)
NaBH_4 , MeOH	TL 261 (1973)
NaBH_4 , $\text{CF}_3\text{CO}_2\text{H}$	Syn 709 (1987)
NaBH_4 , H_2SO_4	Anal Chem 48 484 (1976) Syn 743 (1980)
NaBH_3CN , CH_3CN	JOC 37 1673 (1972); 58 6692 (1993)
NaBH_3CN , HOAc	Syn 709 (1987)
NaBH_3CN , ZnCl_2 , MeOH	JOC 50 1927 (1985)
$\text{MFe}(\text{CO})_4\text{H}$ (M = Na, K)	Syn 733 (1974) BCSJ 49 1378 (1976) JOC 53 1873 (1988)



TL 31 105 (1990)



<u>Reagent</u>	<u>n</u>	
$\text{HFe}(\text{CO})_4^-$	2	Tetr 42 259 (1986)
	3	BCSJ 49 2302 (1976)
	4	J Heterocyclic Chem 25 1383 (1988)
NaBH_3CN	2	JACS 93 2897 (1971); 96 4332 (1974) TL 31 6777 (1990); 32 5183 (1991); 35 2775, 5153 (1994) JOC 59 3175 (1994); 60 4638 (1995)
	3	JACS 93 2897 (1971) JOC 37 1833 (1972); 59 3175 (1994) TL 31 6777 (1990); 32 483 (1991); 35 1833, 2775 (1994); 36 799 (1995)

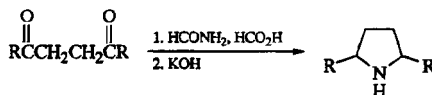
NaTeH

3

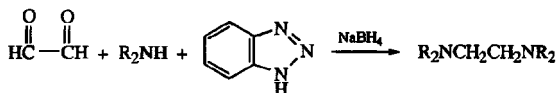
Tetr 49 9605 (1993)

SL 313 (1995)

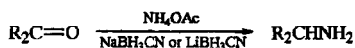
BCSJ 57 3359 (1984)



JOC 53 5383 (1988)



JOC 55 3209 (1990)

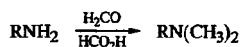
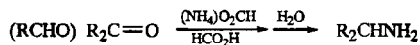


JACS 93 2897 (1971); 107 8066 (1985); 115 10042 (1993)

Syn 135 (1975) (review)

JOC 52 2615, 4274 (1987)

TL 28 773 (1987)

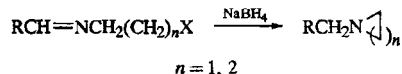


Org Rxs 5 301 (1949) (review)

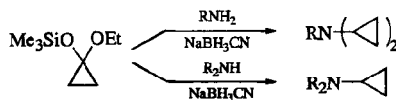
Org Syn Coll Vol 3 723 (1955)

"The Acyclic Aliphatic Tertiary Amines," Macmillan, New York (1965), p 44 (review)

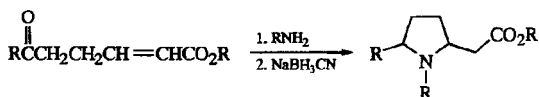
JOC 53 3521 (1988); 60 7364 (1995)



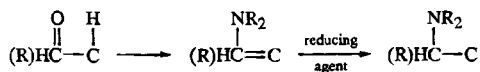
TL 35 8023 (1994)



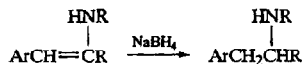
TL 36 7399 (1995)



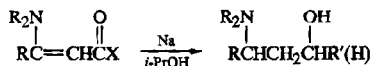
TL 33 2005 (1992)

Reducing agent

H ₂ , cat chiral titanocene	<i>JACS</i> 116 5985 (1994)
H ₂ , cat Pd-C	<i>JOC</i> 54 677 (1989)
H ₂ , cat PtO ₂	<i>Tetr</i> 35 849 (1979) <i>JOC</i> 60 6612 (1995)
Li, NH ₃	<i>Tetr</i> 35 849 (1979)
BH ₃	<i>Tetr</i> 35 849 (1979)
BH ₃ ·NH ₃ , HOAc	<i>JOC</i> 48 3412 (1983)
BH ₃ · <i>t</i> -BuNH ₂ , HOAc	<i>JOC</i> 48 3412 (1983)
BH ₃ ·Me ₂ NH, HOAc	<i>JOC</i> 48 3412 (1983)
BH ₃ · <i>i</i> -Pr ₂ NH, HOAc	<i>JOC</i> 48 3412 (1983)
NaBH ₄ , ROH	<i>Tetr</i> 38 413 (1982) <i>JOC</i> 60 6612 (1995)
NaBH ₄ , HOAc	<i>JOC</i> 28 421 (1963); 48 3412 (1983) <i>Tetr</i> 35 849 (1979)
NaHB(OAc) ₃	<i>JOC</i> 60 4324 (1995)
NaBH ₃ CN, HOAc	<i>J Med Chem</i> 22 341 (1979); 27 386 (1984) <i>JOC</i> 48 3412 (1983)
TiCl ₄ , Et ₃ N/NaBH ₃ CN	<i>TL</i> 31 5547 (1990)
Cl ₂ AlH	<i>Tetr</i> 35 849 (1979)



TL 31 1535 (1990)

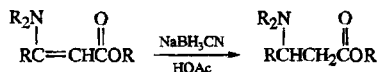


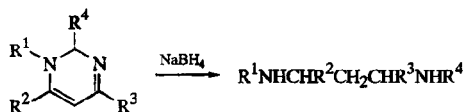
X

R'

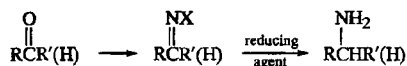
JCS Perkin I 537 (1994)

OR

JOC 59 5328 (1994)*JOC* 59 5328 (1994)



TL 34 1981 (1993)




Review: Org Prep Proc Int 26 193 (1994) (asymmetric reduction)

X
OH

Reducing Agent

H ₂ , Raney Ni	JOC 58 3277 (1993)
H ₂ , cat Pd-C	Org Syn Coll Vol 5 376 (1973)
	BCSJ 57 1040 (1984)
	JOC 54 3211 (1989); 58
	6354 (1993)
	TL 36 825, 4249 (1995)
H ₂ , cat Pd-C, HCl	IACS 50 3370 (1928)
	JOC 53 1064 (1988); 54 2021
	(1989)
H ₂ , cat PtO ₂	JOC 31 1342, 1346 (1966); 37
	335 (1972); 55 2694 (1990);
	57 4386 (1992)
H ₂ O, electrolysis	TL 29 3699 (1988)
Raney nickel	JCS C 531 (1966)
Na, NH ₃ , MeOH	J Gen Chem USSR 35 124
	(1965)
Na, EtOH	Org Syn Coll Vol 2 318 (1943)
Na, n-PrOH	JOC 31 1342, 1346 (1966)
Na(Hg), HOAc	IACS 71 2257 (1949)
Al(Hg), H ₂ O	Angew Int 18 78 (1979)
	IACS 111 6228 (1989)
	JOC 56 4706 (1991)
Zn, HOAc	JOC 57 6324 (1992)
	IACS 117 3976 (1995)
BH ₃	JOC 34 1817 (1969); 51 105
	(1986)
	JCS Perkin I 643 (1979)
BH ₃ , cat PhSO(NH)CH ₂ -	SL 655 (1994)
CPh ₂ OH (enantioselective)	
NaBH ₂ S ₃	Can J Chem 48 735 (1970)
NaBH ₄ , TiCl ₃ , tartaric acid	JOC 54 3750 (1989)
	(α-oximino esters)
NaBH ₄ , TiCl ₄	Syn 695 (1980)
	IACS 115 10042 (1993)
NaBH ₄ , MoO ₃	Chem Ber 117 856 (1984)
	TL 28 5497 (1987)
NaBH ₄ , NiCl ₂ ·6H ₂ O	Ber 117 856 (1984)
AlH ₃	IACS 90 2927 (1968)
	CC 746 (1987)

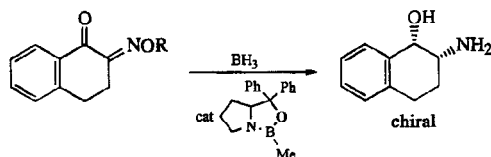
<u>X</u>	<u>Reducing Agent</u>	
	AlH ₃ ·NEt ₃	JOC 58 3974 (1993)
	LiAlH ₄	JOC 17 294 (1952); 50 3948 (1985); 52 4717 (1987); 54 3211 (1989); 59 2114, 5841 (1994)
		J Biol Chem 211 725 (1954)
	NaAlH ₄	CC 746 (1987)
	baker's yeast (enantioselective)	JOC 58 4727 (1993)
		TL 31 5555 (1990)
OCH ₃	Li, NH ₃	JOC 57 4580 (1992)
	H ₂ , cat Pd-C, HCl	JOC 53 1064 (1988)
	BH ₃	JOC 34 1817 (1969); 59 1492 (1994)
	BH ₃ , <i>i</i> -PrCH(NH ₂)CPh ₂ OH (enantioselective)	JCS Perkin I 643 (1979)
	BH ₃ , cat PhSO(NH)CH ₂ -CPh ₂ OH (enantioselective)	BCSJ 60 395 (1987)
	NaBH ₃ (O ₂ CCF ₃)	SL 655 (1994)
		Chem Pharm Bull 26 2897 (1978)
		JOC 54 3436 (1989)
	NaBH ₄	TL 34 5503 (1993)
	Zn(BH ₄) ₂	TL 31 1447 (1990)
	LiAlH ₄	TL 31 1447 (1990)
	LiAlH ₄ ·McN 	JOC 59 1730 (1994)
		TL 35 1515 (1994)
OCH ₂ Ph	H ₂ , cat Pd-C	TL 31 2085 (1990)
	BH ₃	TL 32 711 (1991)
	BH ₃ , cat PhSO(NH)CH ₂ -CPh ₂ OH (enantioselective)	SL 655 (1994)
	(Me ₄ N)HB(OAc) ₃	JACS 114 8750 (1992)
		(β-hydroxy oximes)
	NaBH ₄	TL 31 1447 (1990)
	Zn(BH ₄) ₂	TL 31 1447 (1990)
	LiAlH ₄	JOC 52 3211 (1987)
		JACS 115 10174 (1993)
	Ph ₂ SiH ₂ , Ti(O- <i>i</i> -Pr) ₄	Angew Int 30 585 (1991)
	PhMe ₂ SiH, CF ₃ CO ₂ H	JOC 53 5415 (1988)
OR	NaBH ₃ CN, BF ₃ ·OEt ₂	Angew Int 31 340 (1992)
		JACS 114 10082 (1992)
	BH ₃ , PhCHOHCHMeNH ₂ (enantioselective)	TL 29 223 (1988)
OR, OSiMe ₃	BH ₃ , RCH(NH ₂)CPh ₂ OH (enantioselective)	JCS Perkin I 2039, 2615 (polymer-supported reagent) (1985)
OAc	BH ₃	CC 590 (1967)
	baker's yeast (enantioselective)	TL 31 5555 (1990)

O ₂ CR	PhMe ₂ SiH, CF ₃ CO ₂ H	JOC 53 5415 (1988)
OTs	BH ₃	CC 590 (1967)
	LiAlH ₄	SL 677 (1990)
OMs	LiAlH ₄	SL 677 (1990)
SR (R = Me, Ph)	BH ₃ , cat PhSO(NH)CH ₂ -CPh ₂ OH (enantioselective)	SL 655 (1994)
MgX	NaBH ₄	TL 31 1447 (1990)
	Zn(BH ₄) ₂	TL 31 1447 (1990)
POPh ₂	BH ₃ · <i>t</i> -BuNH ₂ , MeOH; BH ₃ · <i>t</i> -BuNH ₂ , HOAc; NaBH ₄ ; NaBH ₃ CN; LiHB(<i>sec</i> -Bu) ₃ ; or LiAlH ₄	JOC 60 7396 (1995)
	NaBH ₄ /H ⁺	TL 28 5619 (1987)
	LiHB(<i>sec</i> -Bu) ₃ /H ⁺	TL 28 5619 (1987)

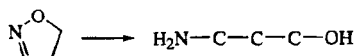
Reducing agent

BH₃, cat PhSO(NH)CH₂CPh₂OH SL 655 (1994)

LiAlH₄-(R) or (S)-bi-2-naphthol; LiAlH₄-1,2(S)-diphenyl-3(R)-methyl-4-(dimethylamino)-2-butanol; or potassium 9-O-(1,2:5,6-di-O-isopropylidene- α -D-glucofuranosyl)-9-boratabicyclo[3.3.1]nonane JOC 52 702 (1987)



TL 36 4337 (1995)



Na, EtOH

Ann 101 (1980)

Na(Hg), ROH, (HOAc)

Ber 84 224 (1951); 97 159 (1964)
Ann 101 (1980)

H₂, cat Pd-C

Ber 97 159 (1964)

BH₃·SMe₂

Ann 101 (1980)

LiBH₄

TL 30 1185, 5969 (1989)

i-Bu₂AlH

JACS 100 7069 (1978)
TL 30 1185 (1989)

LiAlH₄

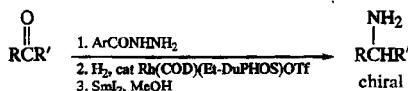
JACS 79 465 (1957); 100 6291 (1978)
 TL 3133 (1978); 23 4777 (1982); 26 2997 (1985); 30
 1185, 5969 (1989)
 Ann 101, 122 (1980)
 Angew Int 20 601, 603 (1981)
 Bull Soc Chim Belg 92 1039 (1983)
 Tetra 40 2199 (1984)
 JOC 57 5403 (1992)

(Me₃O)BF₄/H₂, cat Pd-C

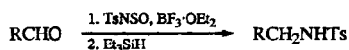
JACS 102 4265 (1980)

(Me₃O)BF₄/NaBH₄ or LiAlH₄/Al(Hg)

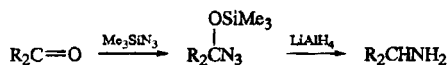
JOC 46 5248 (1981)



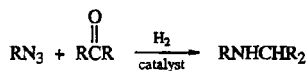
JACS 114 6266 (1992)



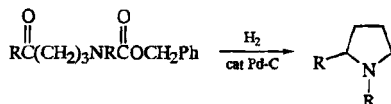
JOC 55 2563 (1990)



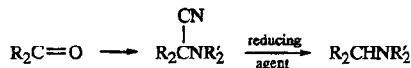
TL 2737 (1977)



See page 815, Section 6.



JOC 54 4088 (1989); 57 5178 (1992)

Reducing agentLi, NH₃, EtOH

TL 28 547 (1987)

Na, NH₃

TL 61 (1976); 23 3369 (1982)
 Chem Pharm Bull 25 2689 (1977)
 SL 878 (1991)

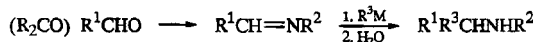
NaBH₄

TL 3105 (1969); 23 3369 (1982)

3. Alkylative Amination

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 1, Part 1.12, p 355

See also page 785, Section 5.



Reviews:

Chem Rev 63 489 (1963)

K. Harada, "The Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 4.3, p 975 (allylic, allenic, propargylic)

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21b, G. Thieme, Stuttgart (1995), pp 1833–1907 (enantioselective)

R³M

RLi

K. Harada, "The Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970), pp 271–272 (review)

JOC 54 5399 (1989)

CL 1555 (1991) (chiral)

SL 961 (1995) (chiral)

RLi (R = alkyl, aryl, vinylic), sparteine or bis(oxazolines) (chiral)

JACS 116 8797 (1994)

RLi (R = 1° alkyl, aryl, vinylic), chiral ligand (chiral)

TL 31 6681 (1990); 32 3095 (1991); 36 7885 (1995)

Tetr Asym 4 1603 (1993)

Tetr 50 4429 (1994)

MeLi

TL 33 235 (1991) (R² = chiral)

JOC 60 2642 (1995)



RC(CH₂)₃Li (R = H, Me)

TL 31 3763 (1990)

CpFe(CO)(PPh₃)COCH₂M (M = Li, AlEt₂)

JACS 106 441 (1984)

t-BuSOCHRLi

JOC 54 2663 (1989)

RCHLiCO₂R

See page 1724, Section 2.

RLi [R = Me, RC≡C, RCOCH₂, RCHNO₂], BF₃·OEt₂

TL 24 4503 (1983)

CH₃CH=CHCH₂M [M = Li, MgCl, B], Sn(*n*-Bu)₃ (BF₃·OEt₂)

JOC 50 3115 (1985) (diastereoselectivity)

RCH=CHCH₂Li(MgX)

BSCF 1832, 1838 (1973)

RC≡CLi

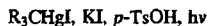
JOC 59 5865 (1994)

$\text{RC}\equiv\text{CLi}$, $\text{BF}_3\cdot\text{OEt}_2$	TL 25 1083 (1984) JOC 59 1396, 5865 (1994)
ArLi	Chem Pharm Bull 30 3160 (1982) JACS 111 6228 (1989) JOC 54 2464 (1989)
RMgX (R = alkyl)	JOC 24 657 (1959); 54 5399 (1989) K. Harada, "The Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970), pp 266-271 (review) Syn 223 (1987) TL 33 235 (1992) (R^2 = chiral); 34 2259 (1993) (chiral); 35 3391 (1994) SL 386 (1993) Tetr 50 1083 (1994) (chiral)
PhCH_2MgCl	Org Syn Coll Vol 4 605 (1963) Chem Pharm Bull 30 3160 (1982)
$\text{H}_2\text{C}=\text{CHCH}_2\text{MgX}$	JOC 24 657 (1959); 54 5399 (1989) TL 32 5865 (1991); 33 3355 (1992); 35 3391 (1994) (chiral) SL 386 (1993)
$\text{H}_2\text{C}=\text{CHMgX}$	Syn 223 (1987)
ArMgX	Syn 223 (1987) JOC 54 5399 (1989) TL 35 3391 (1994) (chiral)
$\text{BF}_3\cdot\text{OEt}_2/\text{RMgBr}$ (R = Et, Ph)	TL 24 4503 (1983)
$\text{BF}_3\cdot\text{OEt}_2/\text{H}_2\text{C}=\text{CHCH}_2\text{MgCl}$	TL 33 3355 (1992)
RMgX (R = 1° alkyl, aryl), 1-trimethylsilylbenzotriazole	JOC 59 7947 (1994); 60 3405 (1995)
$\text{H}_2\text{C}=\text{CHCH}_2\text{MgX}$, CeCl_3	TL 36 8715 (1995)
$\text{H}_2\text{C}=\text{CHCH}_2\text{M}$ [M = MgCl , $\text{B}(\text{OMe})_2$, $\text{B}(\text{C}_6\text{H}_5)_2$, $(\text{AlEt}_3)\text{MgCl}$, $\text{Ti}(\text{O}-i\text{-Pr})_3$, ZnBr]	CC 814 (1985)
$\text{RCH}=\text{CHCH}_2\text{B}(\text{C}_6\text{H}_5)_2$	JACS 106 5031 (1984); 108 7778 (1986) (both chiral) CC 1131 (1985)
$\text{H}_2\text{C}=\text{CHCH}_2\text{B}(\text{OR})_2$	Ann 2000 (1983) JOC 56 365 (1991)
$\text{Me}_3\text{SiCH}=\text{CHCH}_2\text{B}(\text{OR})_2$	JOC 56 365 (1991)
$\text{H}_2\text{C}=\text{C}=\text{CHB}(\text{C}_6\text{H}_5)_2$ (alkyne product)	JOC 60 544 (1995)
$\text{Me}_3\text{SiC}\equiv\text{CCHRB}(\text{C}_6\text{H}_5)_2$ (allenic product) or $\text{Me}_3\text{SiC}(\text{C}_6\text{H}_5)=\text{C}=\text{CHR}$ (propargylic product)	JOC 50 2193 (1985)

$(\text{H}_2\text{C}=\text{CHCH}_2)_3\text{Al}_2\text{Br}_3$	JOC 59 7766 (1994) (chiral)
$\text{CF}_3\text{SiMe}_3, \text{R}_4\text{NF}$	TL 35 3303 (1994) (azirines)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2, \text{SnCl}_4$	SL 51, 629 (chiral) (1990) JOC 56 5883 (1991)
Me_3SiCN	JOC 57 5462 (1992)
$n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CHR}, \text{BF}_3\cdot\text{OEt}_2$	JOC 50 146 (1985); 54 4739 (1989) TL 33 3355 (1992); 34 3223 (1993)
$n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2, \text{Me}_3\text{SiCl}$	TL 36 8649 (1995)
$n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2, \text{SnCl}_4$	SL 629 (1990) (chiral) JOC 56 5883 (1991)
$n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CHR}, \text{TiCl}_4$	JOC 50 146 (1985) TL 34 3223 (1993)
$n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2, \text{cat M}(\text{OTf})_3$ (M = Yb, Sc, La)	TL 36 7289 (1995)
$\text{H}_2\text{C}=\text{CHCH}_2\text{PbBr}\cdot\text{MgClBr}, \text{BF}_3\cdot\text{OEt}_2$	JOC 59 7766 (1994) (chiral)
$(\text{H}_2\text{C}=\text{CHCH}_2)_3\text{Bi}\cdot 3\text{MgCl}_2, \text{BF}_3\cdot\text{OEt}_2$	JOC 59 7766 (1994) (chiral)
$\text{RCH}=\text{CHCH}_2\text{TiX}(\text{O}-i\text{-Pr})_2$ (X = Br, OPh, OCO_2R ; chiral)	JOC 60 8136 (1995)
$\text{Cp}_2\text{TiCHRCH}=\text{CH}_2$	JOMC 224 327 (1982)
Li, naphthalene / $\text{CuCN}\cdot\text{LiCl}$ / allylic chloride	JACS 114 5110 (1992)
$\text{RCu}, \text{BF}_3\cdot\text{OEt}_2$	TL 25 1079 (1984); 31 4175 (1990) CL 1555 (1991) (chiral)
$\text{RC}\equiv\text{CCu}, \text{BF}_3\cdot\text{OEt}_2$	JOC 59 5865 (1994)
$\text{RCu}\cdot\text{MgX}_2, \text{BF}_3\cdot\text{OEt}_2$	TL 33 7783 (1992)
$\text{R}_2\text{CuLi}, \text{BF}_3\cdot\text{OEt}_2$	TL 25 1079 (1984); 30 5611 (1989) CL 1555 (1991) (chiral)
$\text{H}_2\text{C}=\text{CHCH}_2\text{Cu}$	TL 32 1367 (1991) JOC 59 7766 (1994) (chiral)
$(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{CuMgX}$	TL 32 1367 (1991) JOC 59 7766 (1994) (chiral)
$(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{CuMgX}\cdot\text{BF}_3$	TL 32 1367 (1991)
$\text{H}_2\text{C}=\text{CRCH}_2\text{Cu}\cdot\text{ZnI}_2$	JACS 112 6146 (1990)
$t\text{-BuSOCHRZnX}$	JOC 54 2663 (1989)
$\text{RCH}(\text{ZnBr})\text{CO}_2\text{ZnBr}$	See page 1717, Section 1.
$\text{XZnCHRCO}_2\text{R}$	See page 1724, Section 2.
$\text{RCH}=\text{CHCH}_2\text{ZnX}$	BSCF 1832, 1838 (1973) JOC 59 7766 (1994) (chiral)



IOC 59 5865 (1994)

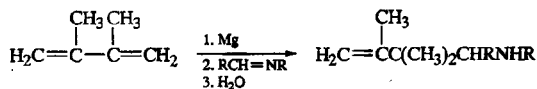


JACS 113 373 (1991)

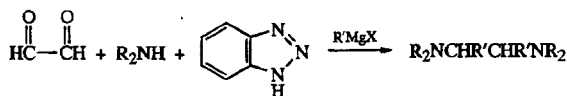


TL 31 4175 (1990)

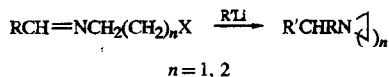
CL 1555 (1991) (chiral)



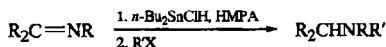
IOC 60 1077 (1995)



IOC 55 3209 (1990)

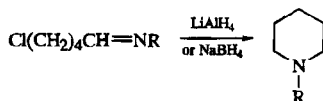


TL 35 8023 (1994)

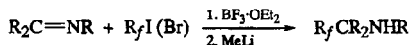


R' = Me, PhCH₂, allylic

IOC 60 2677 (1995)

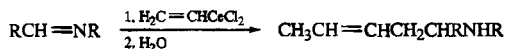


IOC 58 132 (1993)



CL 729 (1988)

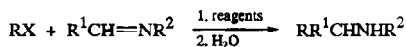
IOC 57 1504 (1992)



TL 36 4043 (1995)



IOC 56 5875 (1991)

RXReagent(s)

electrolysis

TL 30 4161 (1989)

Al(Hg)

JOC 59 7766 (1994) (chiral)

Al, $\text{BF}_3 \cdot \text{OEt}_2$, cat PbBr_2

CL 673 (1987)

Al; cat InCl_3 , SnCl_2 , PbBr_2 ,

JOC 59 7766 (1994) (chiral)

 BiCl_3 or TiCl_4 Al, cat TiCl_4

TL 31 3023 (1990)

In

TL 33 5959 (1992)

JOC 59 7766 (1994) (chiral)

Bi or Ta, $n\text{-Bu}_4\text{NBr}$

TL 34 7975 (1993)

 CrCl_2 , $\text{BF}_3 \cdot \text{OEt}_2$

TL 34 3635 (1993)

Zn

JOC 59 7766 (1994) (chiral)

Zn, cat SnCl_2

JOC 59 7766 (1994) (chiral)

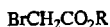
Zn, cat CeCl_3

CC 1542 (1993)

JOC 59 7766 (1994) (chiral)

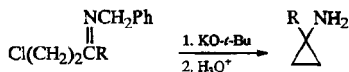
Cd, $n\text{-Bu}_4\text{NBr}$

TL 33 4795 (1992)

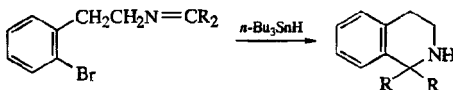


Zn

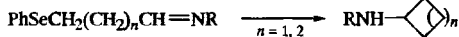
JOC USSR 18 583 (1982)



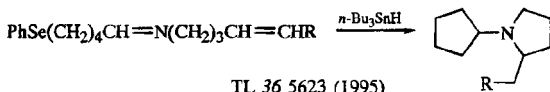
TL 30 5029 (1989)



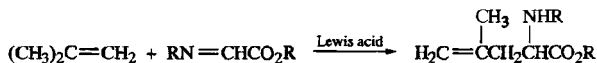
TL 33 2123 (1992)



TL 35 6369 (1994)



TL 36 5623 (1995)



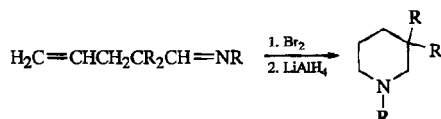
JCS Perkin I 2680 (1981)

JOC 49 5058 (1984); 59 518 (1994)

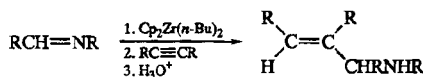
Syn 683 (1985)

CL 1693 (1990)

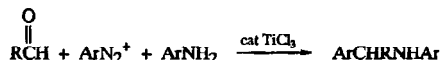
For other ene reactions, see page 236, Section 7.



TL 35 1925 (1994)



See page 440, Section 2.15.



TL 31 2069 (1990)



electrolysis

JCS 101 154 (1912)
 BSCF 4671 (1968)
 TL 1103 (1970); 33 3347 (1992) (intramolecular)
 Ann 1210 (1975)
 SL 51 (1989)
 JOC 56 3063 (1991); 60 3980 (1995) (both intramolecular)

hv

JACS 91 2653 (1969)

Li

JOC 31 453 (1966)
 Can J Chem 44 2497 (1966)

Li, Ph-Ph

JOC 31 453 (1966)

Na

Ber 47 473 (1914)
 JOC 31 453 (1966); 37 653 (1972)
 Can J Chem 44 59, 2497 (1966)
 Syn 489 (1977)

K

Can J Chem 44 2497 (1966)

Mg

JOC 31 453 (1966)

Mg, MgI₂

JACS 53 2672 (1931)
 Arch Pharm 291 248 (1958)

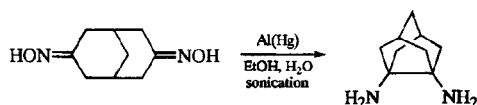
Ba

JOC 31 453 (1966)

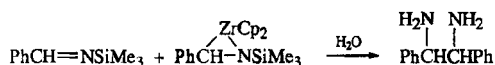
Al-Hg

Ber 41 621 (1908)
 Arch Pharm 286 221 (1953); 303 804 (1970)
 JOC 31 453 (1966); 37 653 (1972)
 Arzneim Forsch 21 2104 (1971)
 J Med Chem 25 832 (1982)
 Helv 70 2215 (1987)

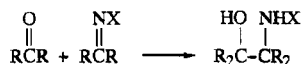
Al-Bi, KOH	TL 36 6747 (1995)
Al, cat PbBr ₂ , AlBr ₃ or CF ₃ CO ₂ H	TL 29 3811 (1988)
In	TL 34 1647 (1993)
TiCl ₄ , K	Helv 70 2215 (1987)
TiCl ₄ , Mg	Helv 70 2215 (1987); 71 1999 (1988)
TiCl ₄ , Mg(Hg)	Syn 255 (1988)
NbCl ₄ (THF) ₂	JACS 109 3152 (1987)
Zn	Syn Commun 10 363 (1980) TL 33 3347 (intramolecular), 5559 (inter- and intramolecular) (1992) JOC 60 3980 (1995) (intramolecular)
Zn, HgCl ₂	Syn Commun 11 61 (1981)
SmI ₂	Syn Commun 20 981 (1990)



TL 35 3187 (1994)

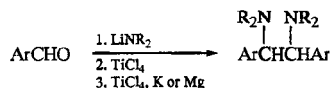


JACS 111 4486 (1989)



X = R, OR

See page 1176, Section 2.2.



Helv 70 2215 (1987); 71 1999 (1988)



electrolysis

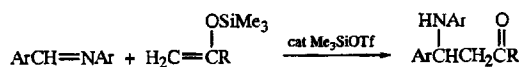
BSCF 4671 (1968)

Mg

Arch Pharm 305 10 (1972)

TiCl₄, Mg

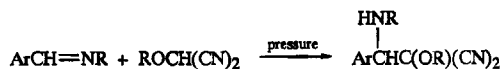
Helv 71 1999 (1988)



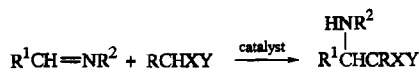
CC 1053 (1987)



JOC 55 6291 (1990)



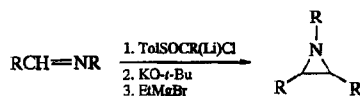
SL 465 (1993)

CatalystX, YHRh(CO)(PPh₃)₃CO₂R, CN; CN, CN

JACS 116 3161 (1994)

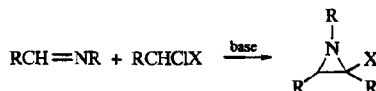
NiX₂(PPh₃)₂ (X = Cl, Br)H, COR; CO₂R, CO₂R

TL 36 5023 (1995)



TL 29 4093 (1988)

JOC 54 3973 (1989)

X

Ar

JOC 60 2279 (1995)

CO₂R

JOC 34 2724 (1969)

CC 602 (1977)

CONR₂

JOC 34 2724 (1969)

CN

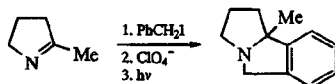
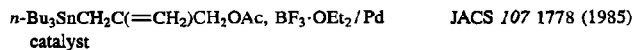
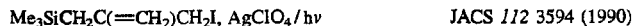
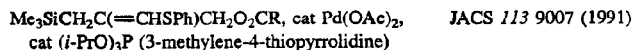
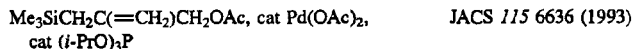
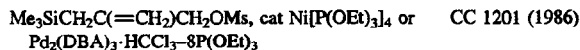
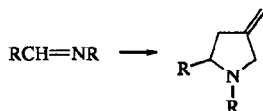
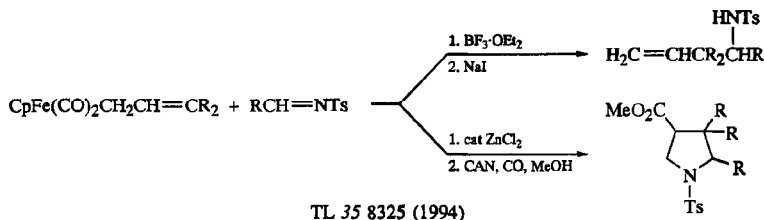
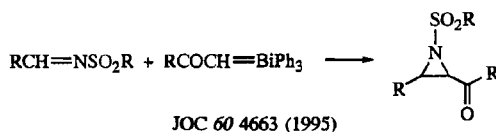
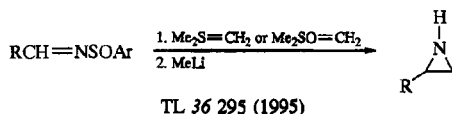
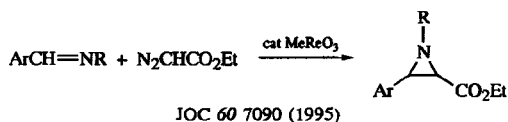
CC 602 (1977)

SO₂Ph

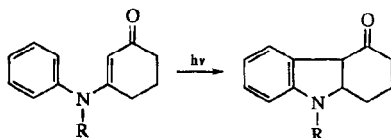
TL 25 1949 (1984)



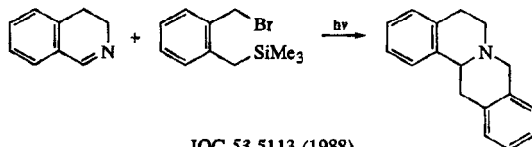
SL 35 (1993)



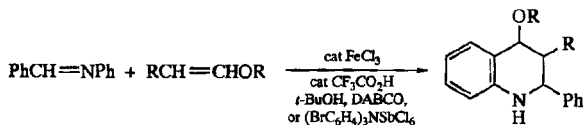
JACS 112 3594 (1990)



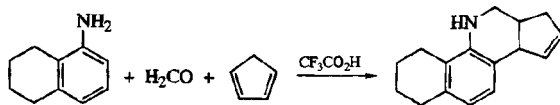
TL 26 2323 (1985); 33 4001 (1992)
J Heterocyclic Chem 25 201 (1988)



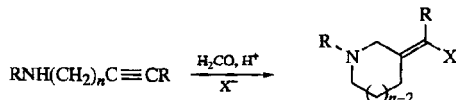
JOC 53 5113 (1988)



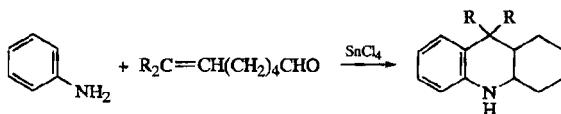
TL 30 7237 (1989)



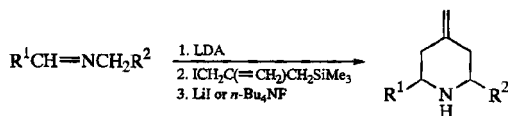
TL 32 7099, 7103 (1991)



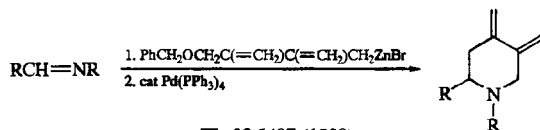
See page 655, Section 4.



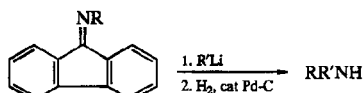
JOC 58 2856 (1993)



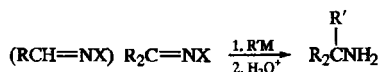
TL 29 4819 (1988)



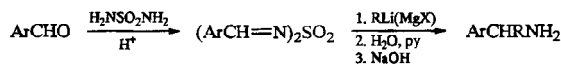
TL 30 5497 (1989)



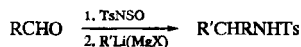
JOC 54 2204 (1989)



$\underline{\text{X}}$	$\underline{\text{R}'\text{M}}$	
OCH ₂ Ph	R'Li	TL 28 4973 (1987)
	R'Li, BF ₃ ·OEt ₂	TL 29 3455 (1988)
		SL 559 (1991)
	R'CeCl ₂	JOC 58 3742 (1993)
SAr	R'Li	JOC 42 398 (1977)
	H ₂ C=CHCH ₂ B(OR) ₂	TL 27 2079 (1986)
SOTol (chiral)	LiCH ₂ CO ₂ R	JOC 60 7037 (1995)
	H ₂ C=CHCH ₂ MgBr	JOC 56 4 (1991)
POPh ₂	R ₂ Zn, amino alcohol (chiral)	CC 1097 (1992)
BH ₂	R'Li, sparteine or chiral polymer (chiral)	Tetr Asym 6 1507 (1995)
Al(<i>i</i> -Bu) ₂	R'Li, sparteine (chiral)	Tetr Asym 6 1507 (1995)
SiMe ₃	R'Li	Syn 461 (1982)
		JOC 48 289 (1983)
		TL 32 2967 (1991)
	R'Li, BF ₃ ·OEt ₂	TL 32 2967 (1991)
	R'Li, sparteine or chiral polymer (chiral)	Tetr Asym 6 1507 (1995)
	R'Li, chiral ligand (chiral)	JCS Perkin I 1341 (1991)
	R'MgX	JOC 48 289 (1983)
		TL 32 2967 (1991)
	R'MgX, R ₃ Al	TL 32 2967 (1991)
	H ₂ C=CHCH ₂ B(OR) ₂ (chiral)	Tetr Asym 6 1531 (1995)
	H ₂ C=CHCH ₂ BR ₂ (chiral)	Tetr Asym 6 1531 (1995)
		Angew 21 203 (1982)
COR	R'Li	
	Et ₂ Zn, PhCHOHCHMe-N(<i>n</i> -Bu) ₂ (chiral)	Tetr Asym 3 437 (1992)
CO ₂ R	RCH=CHCHRSiMe ₃ , BF ₃ ·OEt ₂	JOC 59 2674 (1994)



TL 27 3957 (1986)



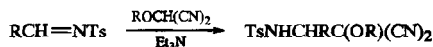
R' = alkyl, allylic, aryl, vinylic, alkynyl

JOC 55 393 (1990); 56 1027 (1991)

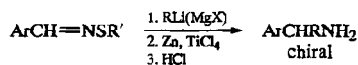


TL 34 7049 (1993)

SL 413 (1994)

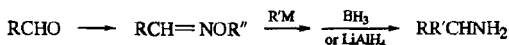


JOC 55 4515 (1990)



R = 1°, 2°, 3° alkyl; allyl

JOC 59 914 (1994)

R'M

RLi

TL 27 3033 (1986)

Can J Chem 71 814 (1993) (chiral)

RLi, BF₃·OEt₂

SL 559 (1991); 445 (1995) (chiral)

Tetr 51 11473 (1995) (chiral)

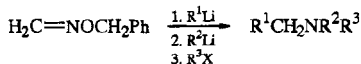
RMgX

TL 27 3033 (1986)

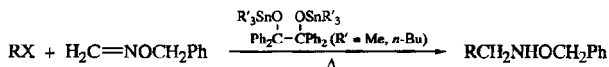
RMgX, BF₃·OEt₂

SL 445 (1995) (chiral)

Tetr 51 11473 (1995) (chiral)



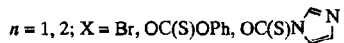
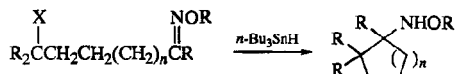
CC 305 (1987)



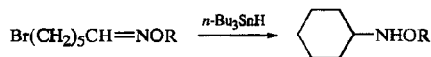
X = Br, I, SePh

JACS 110 1631 (1988)

TL 34 7819 (1993)



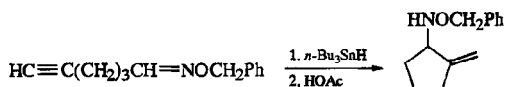
JACS 110 1633 (1988); 117 7289 (1995)



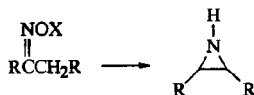
TL 32 6437 (1991)

SL 165 (1991)

JOC 57 403, 2625 (1992); 59 7876 (1994) (ArX)



TL 31 3727 (1990)



Reagent

X

LiAlH₄

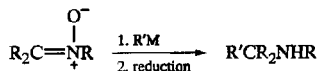
H, Ts

Org Prep Proc 1 305 (1969)
(review)

NaH₂Al(OCH₂CH₂OMe)₂

H, R

JCS Perkin I 1294 (1974)
JOC 53 1761 (1988)



R'M

RLi

JOC 55 3464 (1990) (chiral); 59 6103 (1994)
TL 33 4221 (1992)
SL 78 (1993)

RMgX

JOC 55 3464, 3475 (1990) (both chiral); 59 6103
(1994); 60 5706 (1995)
TL 33 1689 (1992)
SL 78 (1993)

RMgX, chiral ligand

CL 1313 (1993)

R₃B

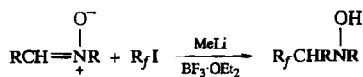
JOC 59 3485 (1994)

ArAlEt₂

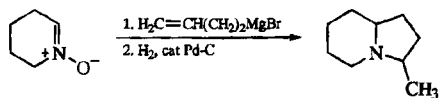
SL 78 (1993)

R₂Zn, chiral ligand

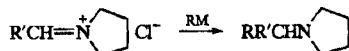
CL 1313 (1993)



JOC 57 1504 (1992)



JOC 60 5803 (1995)

RM

RMgX (R = 1° alkyl)

BSCF II 148 (1983)

RMgX (R = 1°, 2° alkyl)

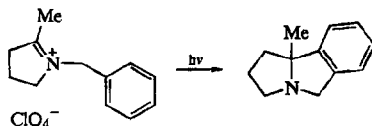
TL 31 797 (1990)

RC≡CMgX

BSCF II 21 (1983)

RMgX (R = 1° alkyl, vinylic, CH₂CO₂R'), RZnX
[R = CH₂COX (X = OEt, NEt₂), CR(CO₂Et)₂]

BSCF II 395 (1982)



JOC 53 1590 (1988)

R'M

RLi

JACS 108 8265 (1986) (chiral)

TL 31 1429 (1990); 32 1171 (1991); 33 1581 (1992)
(all chiral)

JOC 57 4563 (1992) (chiral); 58 3277 (1993)

Syn 1038 (1995) (chiral)

RMgX

JOC 57 4563 (1992) (chiral)

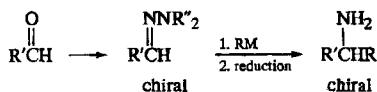
Syn 1038 (1995) (chiral)

RCeX₂

JOC 58 569 (1993)

R₃Ce

Syn 1038 (1995) (chiral)



RM

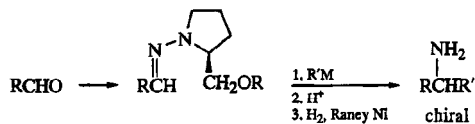
ArLi

Chem Pharm Bull 30 922 (1982)

RMgX

CC 668 (1979)

Chem Pharm Bull 30 922 (1982)

R'M

RLi

Angew Int 25 1109 (1986); 32 418 (1993)

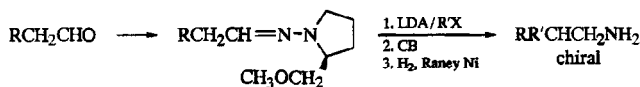
RCECl₂

JACS 109 2224 (1987)

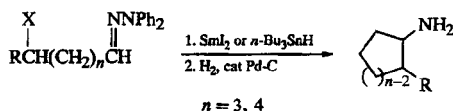
SL 20 (1989); 226, 359 (1993); 795 (1994)

JOC 58 569 (1993)

Angew Int 32 418 (1993)

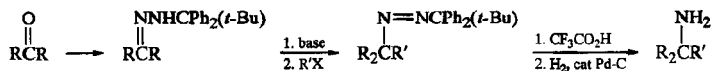


Angew Int 23 365 (1984)

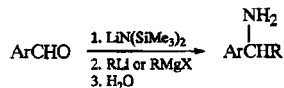


JACS 116 7447 (1994)

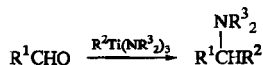
JOC 59 6514 (1994)



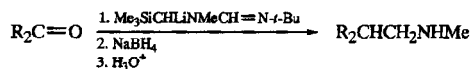
CC 176 (1986)



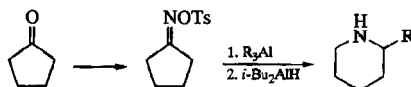
JOC 48 289 (1983); 52 4665 (1987)

 $\text{R}^1 = \text{i-Bu, aryl, vinylic}$

Helv 65 2598 (1982)



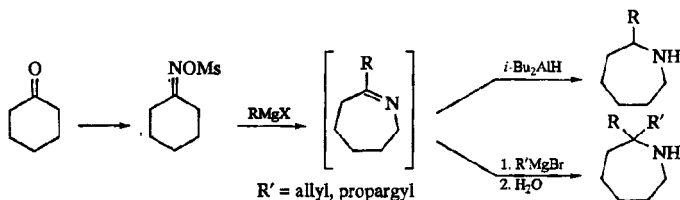
JACS 104 877 (1982)



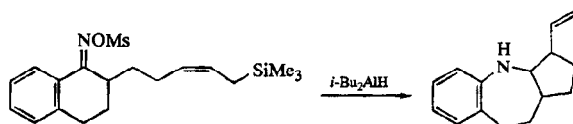
JACS 103 7368 (1981); 105 2831 (1983)

JOC 51 5043 (1986)

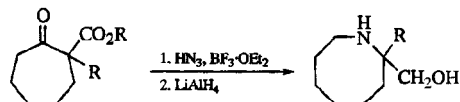
Org Syn Coll Vol 8 568 (1993)



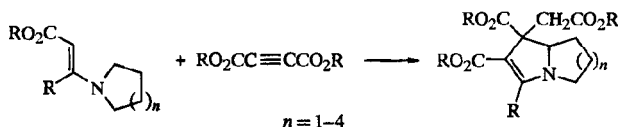
TL 23 3395 (1982)



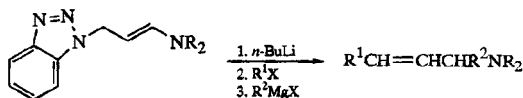
SL 375 (1994)



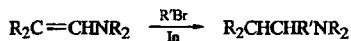
TL 33 17 (1992)



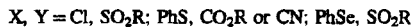
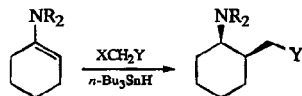
TL 35 1185 (1994)



TL 36 343 (1995)

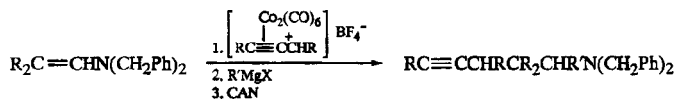


TL 36 6055 (1995)



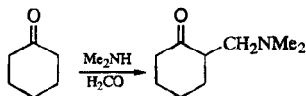
SL 624 (1990) (chiral); 211 (1992)

Angew Int 29 433 (1990)



SL 435 (1992)

4. Mannich and Related Reactions



Reviews:

Org Rxs 1 303 (1942); 7 99 (1953)

Org Syn Coll Vol 3 305 (1955)

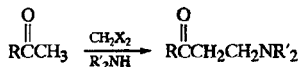
Angew 68 265 (1956)

B. Riechert, "Die Mannich Reaktion," Springer, Berlin (1959)

H. Hellman and G. Opitz, "α-Aminoalkylierung," Verlag Chemie, Weinheim, Germany (1960)

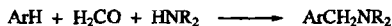
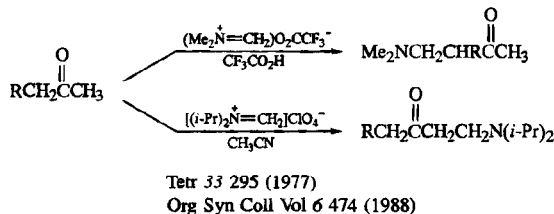
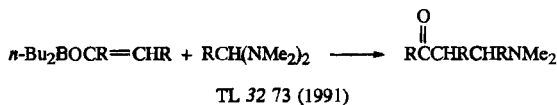
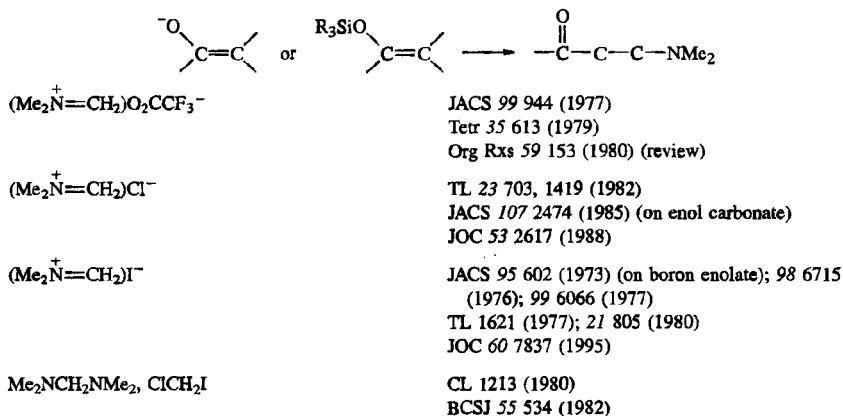
Syn 703 (1973)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 4.1, p 893



Angew Int 21 922 (1982)

BCSJ 55 1331 (1982)



Reviews:

Org Rxs 1 303 (1942)

Syn 703 (1973)

J. Mathieu, J. Weill-Raynal, "Formation of C-C Bonds," G. Thieme, Stuttgart (1973), Vol 1, pp 95-103

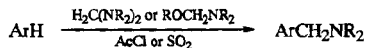
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 4.2, p 953

JACS 70 4232 (1948); 110 6153 (1988)

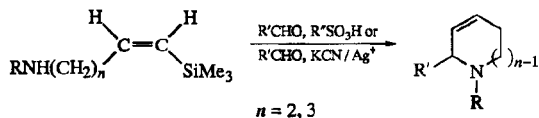
Synthesis 73, 906 (1983)

TL 34 5639 (1993)

JOC 59 2227 (1994)



TL 29 2997, 5801 (1988)

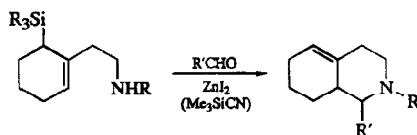
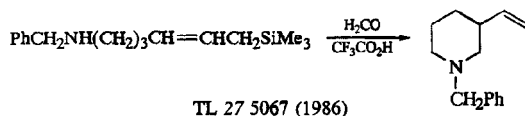
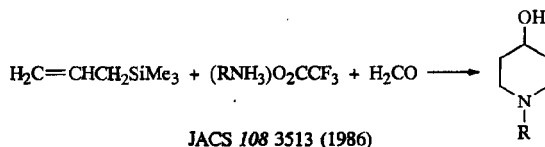


JOC 47 5297 (1982)

JACS 105 6993 (1983); 109 6097, 6107 (1987); 111 300 (1989)

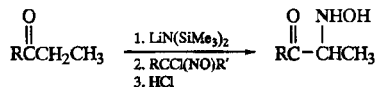
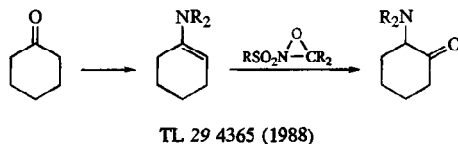
Org Syn Coll Vol 8 358 (1993)

TL 34 5243 (1993)

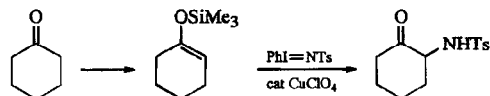


JOC 58 6947 (1993)

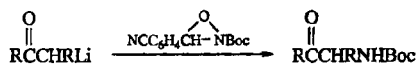
5. α -Amination



JACS 114 5900 (1992)

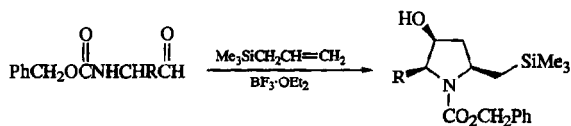


JACS 116 2742 (1994)

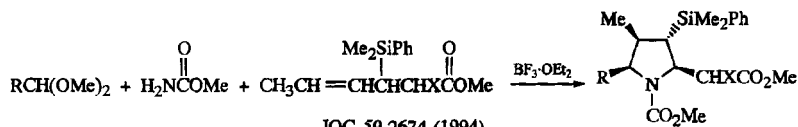


JOC 58 4791 (1993)

6. Miscellaneous Reactions



JOC 59 1958 (1994)

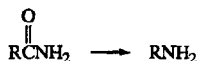


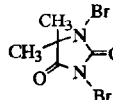
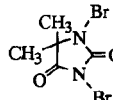
JOC 59 2674 (1994)

11. FROM CARBOXYLIC ACIDS AND DERIVATIVES

1. Molecular Rearrangements

1.1. Hoffman



KBr, electrolysis/ H^+ or OH^-	CL 565 (1982)
NaOX (X = Br, I)	Org Rxs 3 267 (1946) JACS 71 3929 (1949)
NaBrO ₂ , cat NaBr, NaOH	CL 713 (1984)
Br ₂ , NaOMe/ H^+ or OH^-	Syn 290 (1974)
Br ₂ , KOH	JOC 53 3513 (1988)
(PhNMe ₃)Br ₃ , NaOH	CL 463 (1989)
NBS, AgOAc, ROH/ H^+ or OH^-	TL 31 1559 (1990)
NBS, Hg(OAc) ₂ , ROH/ H^+ or OH^-	TL 31 1559 (1990) JOC 59 7774 (1994)
 O, AgOAc, ROH/ H^+ or OH^-	TL 31 1559 (1990)
 O, Hg(OAc) ₂ , ROH/ H^+ or OH^-	TL 31 1559 (1990)
PhIO, HCO ₂ H, H ₂ O	Syn 538 (1983)
PhI(OAc) ₂ , KOH, MeOH/ H^+ or OH^-	JOC 58 2478 (1993)

$\text{PhI}(\text{O}_2\text{CCF}_3)_2/\text{H}^+$ or OH^-

Biochem Biophys Res Commun 80 1 (1978)
JOC 44 1746 (1979); 49 4272, 4277 (1984); 53
5315 (1988)

JACS 103 4508 (1981); 112 5875 (1990)

Org Syn Coll Vol 8 132 (1993)

$\text{PhI}(\text{OH})\text{OTs}/\text{OH}^-$

JOC 51 2669 (1986); 53 5158 (1988)

$\text{Pb}(\text{OAc})_4/\text{R}'\text{XH} (\text{X} = \text{O}, \text{NH})/\text{H}^+$ or OH^-

CC 161 (1965)

TL 4039 (1965); 33 6763 (1992)

JACS 87 1141 (1965)

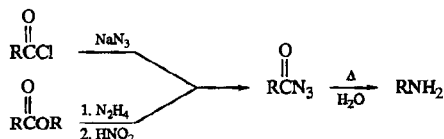
Austral J Chem 21 197 (1968)

JOC 40 3554 (1975); 58 879 (1993); 59 1779, 2179
(1994); 60 6277 (1995)

$\text{Pb}(\text{OAc})_4, \text{RCO}_2\text{H}/\text{H}^+$ or OH^-

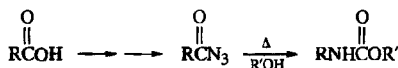
Austral J Chem 21 185 (1968)

1.2. Curtius



Org Rxs 3 337 (1947) (review)

Org Syn Coll Vol 4 819 (1963)



Org Rxs 3 337 (1947) (review)

TL 25 3515 (1984)

JOC 51 3007, 5123 (1986); 52 4875 (1987); 59 7774 (1994)



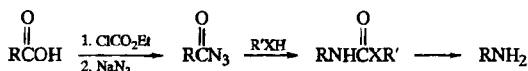
JACS 94 6203 (1972)

Tetr 30 2151 (1974)

Helv 65 1837 (1982)

TL 29 4665 (1988)

JOC 58 879, 1025 (1993); 59 8215 (1994)



$\text{X} = \text{O}, \text{NH}$

JOC 26 3511 (1961); 43 2164 (1978); 53 5315 (1988)

Org Syn Coll Vol 6 95, 910 (1988)

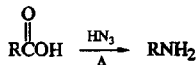
1.3. Lossen



Reagent = SOCl_2 , Ac_2O , P_2O_5 or PPA

Chem Rev 33 242 (1943) (review)

1.4. Schmidt

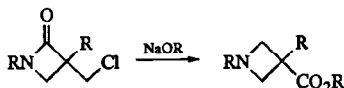


Org Rxs 3 307 (1946) (review)

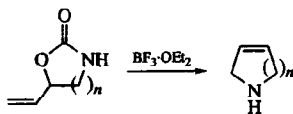
Org Syn Coll Vol 5 273 (1973)

JOC 58 1372 (1993)

1.5. Miscellaneous

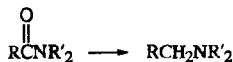


TL 32 4795 (1991)

 $n = 1, 2$

JOC 56 4341 (1991)

2. Reduction of Amides and Imides

 BH_3


JACS 86 3566 (1964); 107 1421 (1985); 111 4859 (1989)

JOC 31 3867 (1966); 33 3637 (1968); 38 912 (1973);
41 149 (1976); 42 4148 (1977); 51 4856, 5373
(1986); 52 5742 (1987); 56 95, 146, 151 (1991);
60 6114 (1995)

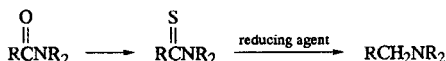
J Heterocyclic Chem 5 875 (1968)

Syn 752 (1978)

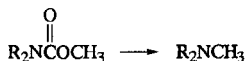
TL 31 1077 (1990); 32 4853 (1991)

BH ₃ ·SMe ₂	Syn 441 (1981) JOC 47 3153 (1982); 57 4470 (1992); 59 2092 (1994); 60 4177 (1995) TL 3315 (1982); 28 4601 (1987) JACS 112 8100 (1990)
BH ₃ ·SMe ₂ ·BF ₃ ·OEt ₂	Syn 996 (1981)
CB	JOC 42 512 (1977)
LiBH ₄	SL 384 (1990)
LiBH ₄ , MeOH, diglyme	JOC 51 4000 (1986)
LiBH ₄ , Me ₃ SiCl	Angew Int 28 218 (1989)
NaBH ₄ , MeOH, <i>t</i> -BuOH	JOC 53 4236 (1988)
NaBH ₄ , CF ₃ CH ₂ OH	JOC 50 3948 (1985)
NaBH ₄ , HOAc	TL 763 (1976) JOC 57 4215 (1992)
NaBH ₄ , MeSO ₃ H	JOC 46 2579 (1981)
NaBH ₄ , py	Chem Pharm Bull 17 98 (1969)
NaBH ₄ , AlCl ₃	JACS 78 2582 (1956)
NaBH ₄ , Me ₃ SiCl	Angew Int 28 218 (1989)
NaBH ₄ , TiCl ₄	Syn 695 (1980)
NaBH ₄ , CoCl ₂ ·6H ₂ O	TL 4555 (1969)
NaBD ₃ (O ₂ CCF ₃)	JACS 110 5791 (1988)
LiBH ₃ CN	JACS 91 3996 (1969)
LiH ₃ BN 	TL 34 1091 (1993)
LiH ₃ BN(<i>i</i> -Pr) ₂	TL 34 1091 (1993) JOC 59 6378 (1994)
NaH ₃ BNMe ₂	JOC 49 2438 (1984)
NaH ₃ BNH- <i>i</i> -Bu	JOC 49 2438 (1984)
AlH ₃	JACS 88 1464 (1966); 90 2927 (1968); 109 6124 (1987)
AlH ₃ ·NMe ₂ Et	JOC 55 2968 (1990)
AlH ₃ ·NEt ₃	JOC 58 3974 (1993)
ClAlH ₂	JOC 56 5263 (1991)
Cl ₂ AlH	JOC 56 5263 (1991)
<i>i</i> -Bu ₂ AlH	Bull Acad Sci USSR, Div Chem Sci 2046 (1959) Ann 623 9 (1959) Syn 617 (1975) JOC 50 2443 (1985); 52 5745 (1987); 56 5263 (1991) SL 384 (1990)

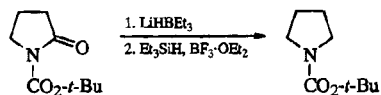
LiAlH ₄	Org Rx 6 469 (1941) (review) Helv 31 1397 (1948); 38 2036 (1955) JOC 18 1190 (1953); 51 3140, 5373 (1986); 52 1844, 2018, 5320 (1987); 53 3190 (1988); 57 4444, 5921 (1992); 59 1904 (1994); 60 4177 (1995) Org Syn Coll Vol 6 382 (1988) SL 501 (1990) TL 35 3687 (1994); 36 5187 (1995)
NaAlH ₄	JOC 58 4727 (1993)
LiAlH ₄ , AlCl ₃	JOC 56 95, 5263 (1991); 57 1656 (1992); 60 6114, 7511 (1995) JACS 113 2652 (1991) (α,β -unsaturated amide) TL 32 4799 (1991)
LiAlH(OMe) ₃	JACS 87 5614 (1965)
NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂	TL 3303 (1968); 30 5227 (1989) JOC 59 1904 (1994)
(Et ₃ O)BF ₄ /NaBH ₄	TL 61 (1968)
(Et ₃ O)BF ₄ /NaBH ₄ , SnCl ₄	Syn 652 (1977)
POCl ₃ /NaBH ₄	TL 219 (1976); 27 2103 (1986) JOC 42 2082 (1977)
POCl ₃ /Zn, EtOH	Experientia 33 101 (1977)
HSCH ₂ CH ₂ SH/NaBH ₄	Chem Ind 322 (1976)

Reducing agent

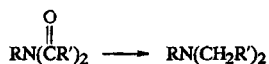
Raney Ni	JOC 16 131 (1951); 55 6236 (1990); 58 6076 (1993) JACS 86 2946 (1964) TL 35 2057 (1994)
MeI/NaBH ₄	JOC 46 3730 (1981)
MeI/NaBH ₃ CN	JOC 46 3730 (1981)
(Et ₃ O)BF ₄ /NaBH ₄	TL 21 4061 (1980); 29 2989 (1988)



BH ₃	JOC 46 2431 (1981)
LiAlH ₄	J Label Compds 6 261 (1970) JOC 46 2431 (1981); 51 3295 (1986); 59 4721 (1994)



TL 35 2055 (1994)

 BH_3 ($\text{R} = \text{H}$)

JOC 53 1114 (1988)

 $\text{NaBH}_4, \text{BF}_3\cdot\text{OEt}_2$ ($\text{R} = \text{Ar}$)

Ann 461 (1979)

3. Reductive Alkylation

 NaBH_4

JACS 96 7812 (1974)

JOC 40 3453 (1975)

Syn 650 (1975); 766 (1978)

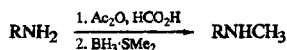
 $\text{BH}_3\cdot\text{NMe}_3$

Syn 1013 (1983)

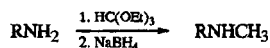


JOC 25 1033 (1960); 27 1042 (1962)

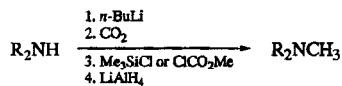
Syn 607 (1975)

 $\text{R} = \text{aryl, alkyl}$

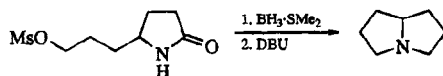
TL 23 3315 (1982)

 $\text{R} = \text{aryl, alkyl}$

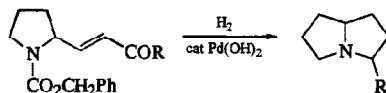
Syn 55 (1974)



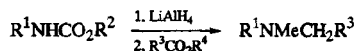
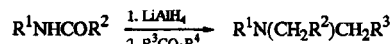
TL 26 5367 (1985)



JOC 59 2906 (1994)



JOC 57 4401 (1992)



TL 3395 (1979)

R'Li/NaBH₃CN (4-alkanellactam)

Heterocycles 24 423, 2315 (1986)

ArLi/BH₃·SMe₂ (5-alkanellactam)

JOC 50 2719 (1985)

(R)ArLi/LiAlH₄ or BH₃·SMe₂ or NaBH₄-CF₃CO₂H (alkanamide, 4- and 5-alkanellactams)

JOC 50 3885 (1985)

(R)ArLi/NaBH₃CN (5-alkanellactam)

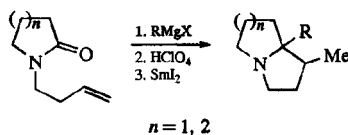
JOC 45 3664 (1980)

R'MgX/NaBH₃CN (4- and 5-alkanellactams)

JACS 107 5534 (1985); III 2588 (1989)

RC≡CBF₂/LiAlH₄ (4-, 5- and 6-alkanellactams)

TL 24 1719 (1983)

 $n = 1, 2$

TL 29 6685 (1988)

MeI/RMgX/NaBH₃CN (4-alkanethiolactam)

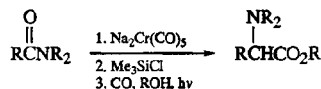
JACS 111 2588 (1989)

MeI/RC≡Cl/NaBH₄ (5-alkanethiolactam)

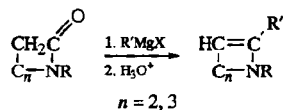
JOC 59 3575 (1994)

RLi (R = alkyl, aryl)/LiAlH₄ (R¹ = aryl)

TL 28 1529 (1987)

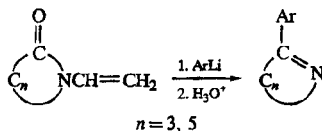


JACS 112 2264 (1990)



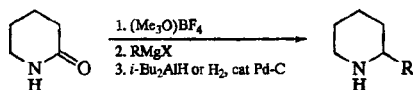
Coll Czech Chem Commun 7 482 (1935); 8 533 (1936)

JACS 55 295, 2543 (1933); 64 2588 (1942); 79 5279 (1957)



Syn 242 (1977)

JOC 47 3652 (1982)

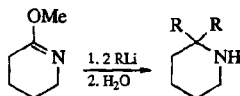


Helv 60 48 (1977)

JOC 60 279 (1995)

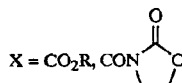
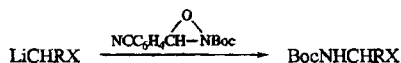


JOC 54 6120 (1989)

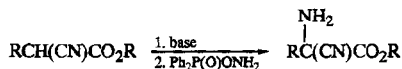


JACS 109 4940 (1987)

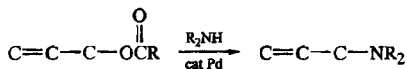
4. Substitution



JOC 58 4791 (1993)



TL 23 5399 (1982); 28 4385 (1987)



See page 789, Section 2.

12. FROM NITRILES



Reviews:

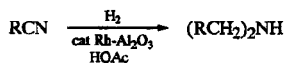
M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 12

M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley & Sons, New York (1978), Chpt 6

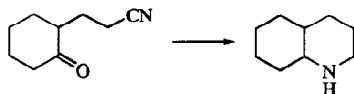
P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 7

H ₂ , cat Rh-Al ₂ O ₃ , NH ₃ , EtOH	JOC 59 2497 (1994)
H ₂ , cat HRh(PPr ⁱ) ₃	CC 870 (1979)
H ₂ , cat Ni	Org Syn Coll Vol 3 229, 358, 720 (1955) JOC 25 1658 (1960) JCS C 531 (1966)
H ₂ , cat Raney Ni	TL 28 6015 (1987) JOC 57 6071 (1992); 58 3736 (1993)
H ₂ , cat Ni-Al-NaOH	TL 30 4879 (1989)
H ₂ , cat Pd	JACS 50 3370 (1928) JCS 426 (1942)
H ₂ , cat Pd-C	JACS 116 1831 (1994)
H ₂ , cat Pd(OH) ₂	JACS 112 6696 (1990)
H ₂ , cat PtO ₂	JOC 37 335 (1972); 58 6804 (1993); 60 946, 1492 (1995) Syn 733 (1981) SL 919 (1991) TL 36 55 (1995)
BH ₃	JACS 82 681 (1960); 110 1679 (1988) JOC 51 4856 (1986); 57 6071 (1992) Org Syn Coll Vol 6 223 (1988) TL 31 2445 (1990); 35 1339 (1994)

$\text{BH}_3 \cdot \text{SMe}_2$	Syn 605 (1981) JOC 47 3153 (1982) TL 35 1339 (1994)
LiBH_4 , MeOH, diglyme	JOC 51 4000 (1986)
LiBH_4 , Me_3SiCl	Angew Int 28 218 (1989)
NaBH_4 , AlCl_3	JACS 78 2582 (1956)
NaBH_4 , Me_3SiCl	Angew Int 28 218 (1989)
NaBH_4 , $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	TL 4555 (1969) Chem Pharm Bull 23 1511 (1975) JACS 104 6801 (1982); 108 67 (1986); 115 4377 (1993); 116 4689 (1994) JOC 55 4528 (1990)
NaBH_4 , cat CuSO_4	SL 419 (1990)
KBH_4 , cat PdCl_2	BSCF 1996 (1959)
$\text{NaBH}_3\text{O}_2\text{CCF}_3$	TL 2875 (1976) JOC 59 5535 (1994)
NaBH_3OH	JOC 42 3963 (1977)
LiHBEt_3 (R = aryl only)	JOC 45 1 (1980)
AlH_3	JACS 88 1464 (1966); 90 2927 (1968)
$\text{AlH}_3 \cdot \text{NMe}_2\text{Et}$	JOC 55 2968 (1990)
$\text{AlH}_3 \cdot \text{NEt}_3$	JOC 58 3974 (1993)
$i\text{-Bu}_2\text{AlH} / \text{NaBH}_4$	JOC 57 3347 (1992)
$i\text{-Bu}_3\text{Al}$	Ann 623 9 (1959)
LiAlH_4	JACS 70 3738 (1948); 77 2544 (1955) Org Rxs 6 469 (1951) (review) JOC 52 2301 (1987); 58 6596 (1993) TL 35 1339 (1994)
NaAlH_4	JOC 58 4727 (1993)
LiAlH_4 , AlCl_3	JACS 77 2544 (1955) Syn 732 (1981); 40 (1987) Chem Pharm Bull 32 873 (1984) JOC 58 6650 (1993)
$\text{LiAl}(\text{OMe})_3$	JACS 87 5614 (1965)
$\text{LaNi}_{4.5}\text{Al}_{0.5}\text{H}_5$	JOC 52 5695 (1987)



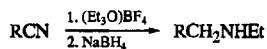
Helv 71 685 (1988)
JOC 56 452 (1991)

H₂, cat Rh-Al₂O₃

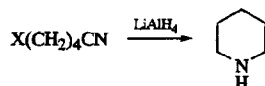
Heterocycles 31 353 (1990)

HCO₂H, cat Pd-C

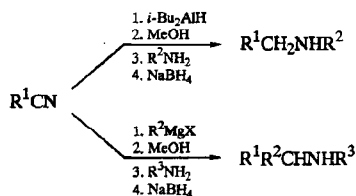
Nouv J Chim 4 199 (1980)



JOC 34 627 (1969)



JOC 58 6451 (1993)



JOC 58 4315 (1993)

R'MReducing agent

R'Li

NaBH₄

TL 30 5137 (1989)

R'MgX

Li, NH₃

JOC 51 5338 (1986)

H₂, Pt catalystJACS 72 876 (1950); 74
4607 (1952)NaBH₄

JACS 109 3378 (1987)

JOC 57 5056 (1992); 58
4315 (1993)LiAlH₄

JACS 75 5898 (1953)

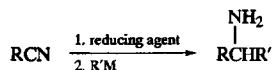
R'MgX, cat CuBr

Li, NH₃

JOC 52 3901 (1987)

R'₂CuLiNaBH₄

TL 30 5137 (1989)

Reducing agentR'MR_nBH_{3-n} (n = 1, 2)

R'Li or R'MgX

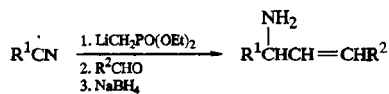
TL 33 627 (1992)

i-Bu₂AlH

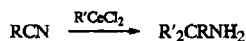
R'Li or R'MgX

JOC 55 4199 (1990)

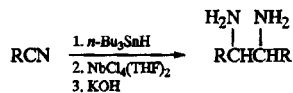
TL 31 3481 (1990)



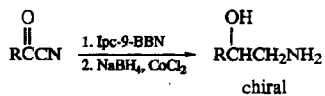
TL 36 281 (1995)



JOC 57 4521 (1992); 60 5295 (1995)



JACS 109 3152 (1987)

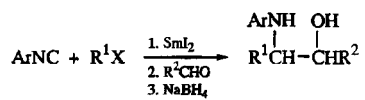


JOC 50 3237 (1985)



See page 792, Section 3 for this and related reactions.

13. FROM ISONITRILES



JOC 58 6766 (1993)

ETHERS

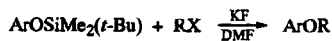
GENERAL REFERENCES

- A. Resowsky, "The Chemistry of Heterocyclic Compounds," Interscience, New York (1964), Vol 19, Part 1 (epoxides)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/3, G. Thieme, Stuttgart (1965): ethers, p 1; epoxides, p 367; oxetanes, p 489; tetrahydrofurans, p 517
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/4 (cyclic ethers), G. Thieme, Stuttgart (1966)
- "The Chemistry of the Ether Linkage," Ed. S. Patai, Interscience, New York (1967)
- Supplement E: "The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and their Sulphur Analogues," Parts 1 and 2, Ed. S. Patai, J. Wiley, New York (1980)
- Tetr 39 2323 (1983) (Recent Advances in the Preparation and Synthetic Applications of Oxiranes); 43 3309 (1987) (Synthetic Routes to Tetrahydrofuran, Tetrahydropyran, and Spiroketal Units of Polyether Antibiotics and a Survey of Spiroketal of Other Natural Products); 50 8885 (1994) (Chemical and Biological Synthesis of Chiral Epoxides)
- Syn 629 (1984) (Synthetically Useful Reactions of Epoxides)
- "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 6, Part 1.1, p 1
- "The Chemistry of Hydroxyl, Ether and Peroxide Groups," Ed. S. Patai, Supplement E2, J. Wiley, Chichester, U.K. (1993)
- Contemporary Organic Synthesis 1 457 (1994) (Recent Developments in the Synthesis of Medium-Ring Ethers)

1. FROM OTHER ETHERS

See also page 889, Section 2 and page 912, Section 4.

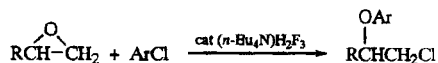
For the kinetic resolution of chiral epoxides, see: TL 27 1359 (1986); 29 1417 (1988)



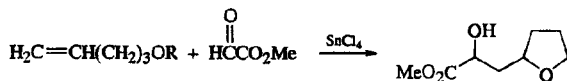
TL 28 4139 (1987)



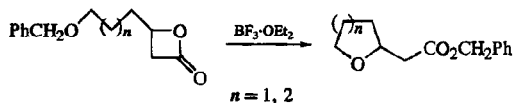
JACS 110 7737 (1988)



SL 853 (1995)

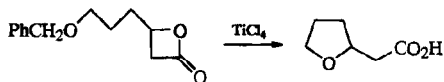


TL 33 6315 (1992)

 $n = 1, 2$

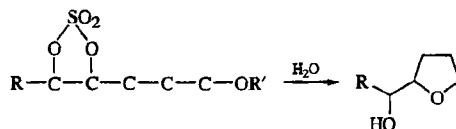
TL 29 6573 (1988)

JOC 55 2991 (1990)



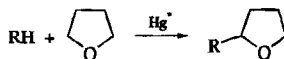
TL 30 6829 (1989); 36 1205 (1995)

JOC 55 2991 (1990); 57 2511 (1992)

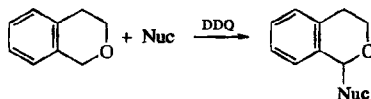


R' = PhCH₂, CH₃OCH₂, *t*-Bu, *t*-BuMe₂Si

JACS 117 12873 (1995)

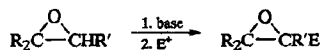


JACS 111 2946 (1989)



Nuc = enol silane, RLi(MgX), H₂C=CHCH₂M (M = SiR₃, SnR₃), Me₃SiCN

TL 34 8189 (1993)



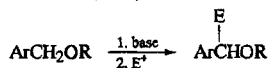
R' = Ar, CH=CH₂, C≡CR, CO₂R, CN, SO₂R, PO(OR)₂, SiR₃

E⁺ = D₂O, RX, RCONR₂, CO₂, R₃SiCl, R₃SnCl

JOMC 121 C10 (1976); 341 293 (1988)

JACS 98 4646 (1976)

IOC 55 4835 (1990)



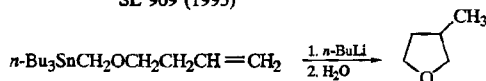
E⁺ = RX, epoxide, R₂CO, RCO₂Et

TL 4155 (1979); 36 5641 (1995)

JCS Perkin I 1652 (1981)

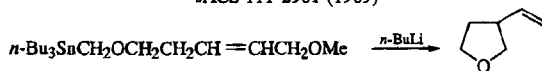
JOMC 379 81 (1989)

SL 909 (1993)

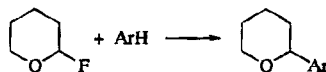


IOC 53 1336 (1988)

JACS 111 2981 (1989)



IOC 53 1336 (1988)



$\text{BF}_3 \cdot \text{OEt}_2$	SL 709 (1991)
$\text{Cp}_2\text{ZrCl}_2, \text{AgClO}_4$	TL 30 833 (1989)
$\text{Cp}_2\text{HfCl}_2, \text{AgClO}_4$	TL 29 6935 (1988); 30 6185 (1989)
	SL 709 (1991)
	JACS 113 6982 (1991)



X = halogen

RM

PhLi , cat Ph_2TiBr TL 32 2255 (1991)

$\text{RC}\equiv\text{CLi}$, cat Me_2TiCl TL 32 2255 (1991)

RMgX Ber 97 636 (1964)
 Angew Int 6 335 (1967) (review)
 TL 28 2225 (1987)
 Org Syn Coll Vol 6 675 (1988)
 JOC 53 4026 (1988); 59 7238 (1994)

ArMgX , cat Li_2CuCl_4 TL 31 6953 (1990)

RAlEt_2 (R = 2-furyl, 2-pyrrolyl) JOC 53 3371 (1988)

$\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$, cat Me_3SiX (X = I, OTf) CL 409 (1983)

Ph_3Ti SL 235 (1991)

$\text{RC}\equiv\text{CTiMe}_2$ SL 235 (1991)

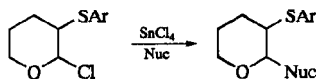
Cp_2ZrCl_2 , cat CuCl JOC 60 6260 (1995)

$\text{RCH}=\text{CHZrClCp}_2$, ZnCl_2 JOC 60 6260 (1995)

R_2CuLi TL 28 2225 (1987)
 JOC 53 4026 (1988)

Ar_2Zn TL 36 1795 (1995)

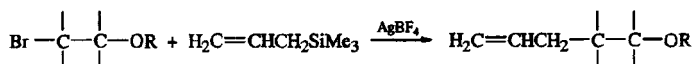
Ar_2Cd TL 36 1795 (1995)



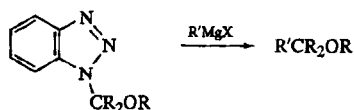
Nuc = Me_3SiCN , $\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$, $\text{C}=\text{COR}$

(R = Me, SiMe₃), $\text{R}_2\text{C}=\text{C}(\text{OR})\text{OSiMe}_3$, PhMgX

TL 34 3047 (1993)

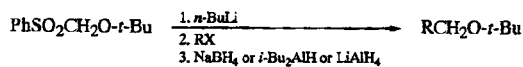


JOC 48 1557 (1983)

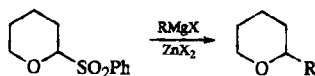


R' = alkyl, PhCH₂, aryl

JOC 54 6022 (1989)



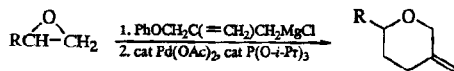
SL 503 (1991)



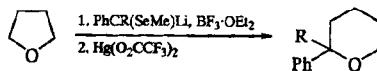
R = aryl, vinylic, alkynyl, allylic

TL 29 4869 (1988); 35 319 (1994)

SL 749 (1990)



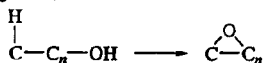
TL 30 4863 (1989)



SL 320 (1992)

2. ALKYLATION OF ALCOHOLS AND PHENOLS

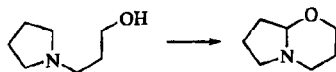
See also page 912, Section 4 and page 928, Section 7.



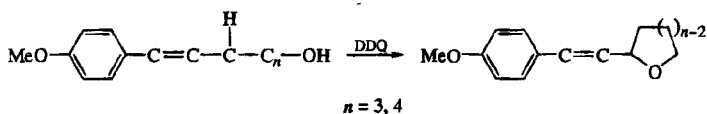
Review: Syn 501 (1971) (hypiodite reaction)

Reagent(s)	<i>n</i>	
Cl ₂ , Ag ₂ CO ₃	3	Tetr 29 3675 (1973)
Cl ₂ , HgO	3	Tetr 29 3675 (1973)
Br ₂ , AIBN	3	TL 29 85 (1988)
Br ₂ , AgOAc	3	TL 1049 (1973) Tetr 29 3675 (1973) JOC 47 3559 (1982)
Br ₂ , Ag ₂ CO ₃	3	Tetr 29 3675 (1973)
Br ₂ , Ag ₂ O	3	JACS 86 3905, 5503 (1964) JOC 30 3216 (1965) CC 981 (1969); 976 (1970); 451 (1973) Tetr 29 3675 (1973)
Br ₂ , HgO	3	Tetr 29 3675 (1973)
I ₂ , HgO	3, 4	JACS 87 1807 (1965); 109 8117 (1987) CC 981 (1969) TL 24 5915 (1983); 25 2035 (1984); 28 4951 (1987)
I ₂ , Pb(OAc) ₄ , hv	3	TL 29 2727, 2761 (1988); 32 6203 (1991)
I ₂ , PhI(OAc) ₂ , hv	3	TL 26 2115 (1985); 31 3043 (1990); 35 1503 (1994) JCS Perkin I 125 (1988) JOC 59 6395 (1994)
I ₂ , Ph ₂ Se(OH)OAc, hv	3	JOC 59 6395 (1994)

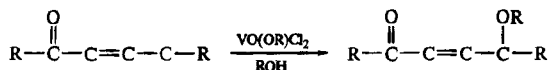
Reagent(s)	<i>n</i>	
NIS, hv	3	JOC 48 3126 (1983); 50 3015 (1985) TL 30 4791 (1989)
DDQ	3, 4	TL 28 5175 (1987)
Pb(OAc) ₄ , Δ or hv	3, 4	TL 3975 (1964) Tetr 25 2269 (1969) JOC 57 3214 (1992)



hv, 1,4-dicyanonaphthalene	TL 29 4153 (1988); 32 5147 (1991)
hv, R ₂ CO	TL 35 1715 (1994)
ClO ₂	IACS 110 4829 (1988)
Hg(OAc) ₂	IACS 82 5148 (1960); 110 4829 (1988)



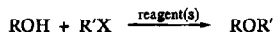
Heterocycles 23 553 (1985)



TL 32 1741 (1991)

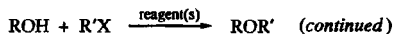


TL 35 6453 (1994)



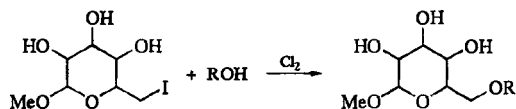
Reagent(s)	R'X	
—	MeOTf	IACS 115 2042 (1993)
—	PhCH ₂ OTf	Carbohydr Res 35 C4 (1974)
—	1°, 2° alkyl bromide; 1° alkyl iodide	JOC 48 1360 (1983)
—	[(R'O) ₃ PCH ₃]BF ₄	JOC 49 4877 (1984)
—		Ber 99 1479 (1966)

—	PhCH ₂ Cl	Adv Carbohydr Chem 12 137 (1957) (review)
hν	R ₃ CBr(I)	JACS 113 2709 (1991)
microwave irradiation	1° alkyl bromide	JOC 60 2456 (1995)
<i>n</i> -BuLi	HC≡CCH ₂ Br	JACS 111 5312 (1989)
Na	PhCH ₂ Cl(Br)	JACS 63 3244 (1941)
NaH	MeI	Carbohydr Res 2 162 (1966) Methods Carbohydr Chem 6 376, 378 (1972) TL 21 (1973) Syn 434 (1974) JACS 109 3353 (1987); 110 577 (1988); 112 4528 (1990) Can J Chem 41 1801 (1963) JCS 5391 (1964) JOC 54 3757 (1989)
	PhCH ₂ Cl	
	1° alkyl bromides and iodides, PhCH ₂ Cl	
	ROTs (1° alkyl)	JOC 53 5034 (1988)
	ROTF (1° alkyl)	JACS 115 12550 (1993)
NaH, DMF	PhCH ₂ Br	JCS 5614 (1964) Methods Carbohydr Chem 6 376 (1972) JOC 52 4665 (1987) Carbohydr Res 2 167 (1966)
	RBr	
NaH, HMPA	1° alkyl bromide and iodide, PhCH ₂ Cl	BSCF 1866 (1965)
NaH, <i>n</i> -Bu ₄ NBr	PhCH ₂ Br	JACS 115 10167 (1993)
NaH, <i>n</i> -Bu ₄ NI	PhCH ₂ Br	JACS 115 12550 (1993)
NaOH	Me ₂ SO ₄	Acta Chem Scand 16 2005 (1963)
NaOH, C ₆ H ₆	MeCl, Me ₂ SO ₄	Syn 123 (1979)
NaOH, DMSO	MeI, PhCH ₂ Br PhCH ₂ Cl	TL 36 2952 (1995) Methods Carbohydr Chem 6 368, 378 (1972)
NaOH, <i>n</i> -Bu ₄ NI	Me ₂ SO ₄	Angew Int 12 846 (1973)
NaOH, (PhCH ₂ NEt ₃)Cl	allylic bromide, benzylic bromide, 1° alkyl tosylate	SL 171 (1994)
NaOH, cat (<i>n</i> -Bu ₄ N)HSO ₄	1° alkyl chloride, benzylic chloride, BrCH ₂ CO ₂ R	TL 3251 (1975); 28 4143 (1987)
NaCH ₂ SOCH ₃ , DMSO	MeI	J Biochem (Tokyo) 55 205 (1964) Biochem 5 1508 (1966) Methods Carbohydr Chem 6 361 (1972)

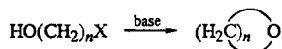


Reagent(s)	R'X	
KOH	PhCH ₂ Cl	Ber 70 1848 (1937); 93 556 (1960) Can J Chem 41 1801 (1963)
KOH, THF	PhCH ₂ Cl Me ₂ SO ₄	JOC 28 2999 (1963) JOC 54 3984 (1989)
KOH, dioxane	PhCH ₂ Cl	Methods Carbohydr Chem 6 373 (1972)
KOH, DMSO	1° alkyl bromide and iodide R ₂ SO ₄ (R = Me, Et)	Tetr 35 2169 (1979) Syn 428 (1979)
KOH, (PhCH ₂ NEt ₃)Cl, CH ₂ Cl ₂	allylic chlorides, HC≡CCH ₂ Br	TL 35 6477 (1994)
K ₂ CO ₃ , KI, CH ₃ CN	2,4-Me ₂ C ₆ H ₃ CH ₂ Cl	Syn 987 (1982)
KF, alumina	1° alkyl iodide, PhCH ₂ Br	BCSJ 55 2504 (1982)
alumina	Me ₂ SO ₄	BCSJ 59 2481 (1986)
n-Bu ₂ SnO, n-Bu ₄ NBr	PhCH ₂ Br	TL 30 6075 (1989)
py	Ph ₃ CBr p-MeOC ₆ H ₄ CPh ₂ Cl	JOC 44 1438 (1979) JOC 44 1438 (1979)
py, DMAP	Ph ₃ CCl	JACS 111 1861 (1989)
2,6-di- <i>tert</i> -butylpyridine or 1,2,2,6,6-pentamethyl- piperidine	ROTF (1° alkyl)	TL 35 5075 (1994)
2,6-di- <i>tert</i> -butyl-4-methyl- pyridine	MeOTf PhCH ₂ OTf	TL 35 7171 (1994) TL 29 4393 (1988)
1,8-bis(dimethylamino)- naphthalene	ROTF (Me ₃ O)BF ₄	JOC 59 2945 (1994) TL 35 7171 (1994) JOC 59 3113 (1994)
DBU	Ph ₃ CCl	TL 33 2689 (1992)
cat Ni(acac) ₂	1° alkyl bromide, benzylic chloride	Syn 803 (1977)
Ag ₂ O	MeI, EtX (X = Br, I), PhCH ₂ X (X = Cl, Br)	JCS 83 1021, 1037 (1903) JACS 73 4043 (1951); 108 4603 (1986); 109 6124 (1987); 110 5768 (1988) Acta Chem Scand 13 593 (1959); 16 2005 (1963) JOC 26 4553 (1961); 27 290 (1962); 52 3889, 4647 (1987) JCS C 2372 (1969)

		TL 28 4019, 5353 (1987) Org Syn Coll Vol 7 386 (1990)
Ag ₂ CO ₃	H ₂ C=CHCH ₂ I	JACS 111 989 (1989)
AgOTf	3° alkyl chloride 3° alkyl bromide	JACS 110 1303 (1988) JACS 110 8591 (1988)
AgOTf, 2,6-di- <i>i</i> -butylpyridine	1° alkyl iodide, PhCH ₂ Cl, H ₂ C=CHCH ₂ Br	TL 35 8111 (1994)
AgBF ₄ , Ag ₂ CO ₃	1° alkyl iodide	JOC 53 5034 (1988)
H ⁺	Cl ₃ CC(=NH)OCH ₂ Ph (R' = CH ₂ Ph)	CC 1240 (1981) JACS 110 1624 (1988) TL 32 1613, 1749 (1991) JOC 56 417 (1991); 57 5292 (1992); 58 7768 (1993); 59 3113 (1994)
BF ₃ ·OEt ₂	Cl ₃ CC(=NH)OR'	TL 29 2483 (1988) JOC 54 3738 (1989)



TL 35 2335 (1994)



"Heterocyclic Compounds," Ed. R. C. Elderfield, J. Wiley, New York (1950), Vol 1, p 8

JACS 72 1593 (1950); 75 4778 (1953); 110 531 (1988)

JOC 36 943 (1971); 52 3860, 3883 (1987); 53 5534 (1988); 57 1405, 3380 (1992); 58 486 (1993)

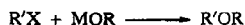
 Topics Stereochem 7 93 (1973) (review, *n* = 2)

Acct Chem Res 14 95 (1981)

 TL 28 723, 1781, 2709 (1987); 29 6107 (1988); 33 6735 (1992); 34 5093, 5227 (1993); 36 4765, 5453, 7367
(1995)

Org Syn Coll Vol 8 434 (1993)

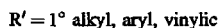
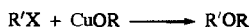
SL 927 (1993)


 Review: "The Chemistry of the Ether Linkage," Ed. S. Patai, Interscience, New York (1967),
pp 445-498

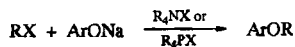
JACS 69 2451 (1947)

JCS 616 (1948)

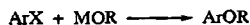
JOC 43 4682 (1978); 52 4495 (1987)



JACS 96 2829 (1974)

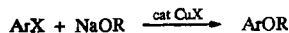


TL 33 4435 (1992)
JOC 59 4683 (1994)

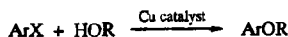


M = Na, K

Org Syn Coll Vol 5 926 (1973)
JACS 110 119 (1988)
TL 31 55 (1990); 34 999 (1993)



JCS C 312 (1969)
TL 34 1007 (1993)
JOC 59 406 (1994)

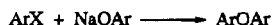


Tetr 40 1433 (1984) (review)



- K₂CO₃ JOC 57 4765 (1992); 59 5535 (1994)
(intramolecular)
TL 34 999, 7741 (1993); 35 5649 (1994); 36 1279
(1996) (intramolecular)
- K₂CO₃, 18-crown-6 JOC 60 6389 (1995) (intramolecular)
TL 36 1279 (1995) (intramolecular)
- K₂CO₃, CuO, py Chem Pharm Bull 13 1341 (1965)
TL 29 3227 (1988)
JOC 53 72 (1988); 59 5414 (1994)
JACS 111 1063 (1989)
SL 49 (1994)
- K₂CO₃, CuO, Cu, py SL 433 (1994)
- K₂CO₃, CuBr·SMe₂, py TL 35 4409 (1994)
- KO-*t*-Bu, DMSO JOC 47 4374 (1982)
- KO-*t*-Bu, electrolysis JOC 55 6347 (1990)
- NaH TL 35 5649 (1994)
- NaH, CuBr·SMe₂ TL 30 2053 (1989)
JOC 54 2498 (1989); 55 6000 (1990); 56 1763, 4204
(1991) (both intramolecular); 58 1425 (1993)
(intramolecular)
JACS 113 1427 (1991); 115 3420, 11426 (1993) (all
intramolecular)

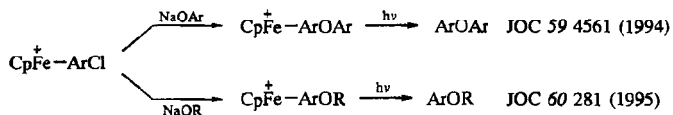
NaH/CuCl, 18-crown-6	TL 30 4211 (1989)
KF, Al ₂ O ₃ , 18-crown-6	JOC 58 3229 (1993)
CsF	TL 35 5649 (1994); 36 1279 (1995) (intramolecular)
MeCu, py	JOC 56 4204 (1991); 58 1425 (1993) (both intramolecular)
Tl(NO ₃) ₃	TL 30 6043 (1989) (intramolecular)
Tl(NO ₃) ₃ /Zn, HOAc	CL 1851 (1982) TL 27 4481 (1986); 29 559 (1988); 30 379 (1989) (all intramolecular)



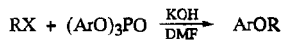
Cu	Org Syn Coll Vol 2 445 (1943) Chem Rev 38 405 (1946) (review) JOC 29 3624 (1964); 32 2501 (1967) Tetr 40 1433 (1984) (review) JACS 116 3680 (1994)
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CuBr·SMe ₂	TL 33 4799 (1992)
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CuI	TL 35 1769 (1994)
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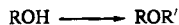


TL 31 2017 (1990)



RX = 1° RBr, PhCH₂Br, ArCl

Syn 828 (1982)

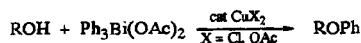


CH ₂ N ₂ , silica gel	TL 4405 (1979)
CH ₂ N ₂ , cat HBF ₄	JACS 80 2584 (1958) Tetr 6 36 (1959)
CH ₂ N ₂ , cat BF ₃ ·OEt ₂	JACS 80 2584 (1958) Angew 70 105 (1958) Carbohydr Res 3 177 (1966); 4 432 (1967) Methods Carbohydr Chem 6 365 (1972)

CH_2N_2 or CH_3CHN_2 , cat $\text{BF}_3 \cdot \text{OEt}_2$	<i>Z Naturforsch B</i> 14 209 (1959)
$\text{Me}_3\text{SiCHN}_2$, HBF_4 ($\text{R}' = \text{Me}$)	<i>TL</i> 31 5507 (1990)
RCHN_2 , cat AlCl_3 or $\text{BF}_3 \cdot \text{OEt}_2$	<i>Ann</i> 677 55 (1964)
PhCHN_2 , cat HBF_4	<i>TL</i> 30 4759 (1989)
RCOCHN_2 , cat $\text{BF}_3 \cdot \text{OEt}_2$	<i>JACS</i> 72 5161 (1950)
$\text{RC}(\text{N}_2)\text{CO}_2\text{R}$, cat $\text{Rh}_2(\text{OAc})_4$	<i>TL</i> 35 3139, 5949, 6709 (intramolecular) (1994) <i>SL</i> 1191 (1995) <i>JOC</i> 60 4449 (1995)
N_2CXY [$\text{X}, \text{Y} = \text{COR}, \text{SO}_2\text{Ph}$ (intramolecular); $\text{CO}_2\text{Et}, \text{CO}_2\text{Et}; \text{CO}_2\text{Et}, \text{SO}_2\text{Ph}; \text{CO}_2\text{Et}, \text{PO}(\text{OEt})_2$; $\text{SO}_2\text{Ph}, \text{SO}_2\text{Ph}; \text{SO}_2\text{Ph}, \text{PO}(\text{OEt})_2$], cat $\text{Rh}_2(\text{NHCOCF}_3)_4$	<i>SL</i> 975 (1992)



JOC 42 1801 (1977)

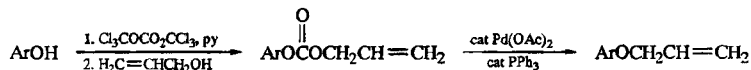


J Gen Chem USSR 55 2232 (1985)



$\text{MeI}, \text{K}_2\text{CO}_3, \text{DMF}$	<i>JOC</i> 59 3775 (1994)
$\text{MeI}, \text{KOH}, \text{DMSO}$	<i>Tetr</i> 35 2169 (1979)
$\text{MeI}, \text{NaOH}, \text{HMPA}$	<i>JOC</i> 39 1968 (1974)
$\text{Me}_2\text{SO}_4, \text{NaOH}$	<i>Org Syn Coll Vol</i> 1 58 (1941)
$1^\circ \text{RBr}, \text{K}_2\text{CO}_3$	<i>Org Syn Coll Vol</i> 3 140 (1955)
RX ($1^\circ \text{RCl}, \text{RBr}, \text{RI}; 2^\circ \text{RBr}$), $\text{KF} \cdot \text{Al}_2\text{O}_3$	<i>CL</i> 755 (1959) <i>BCSJ</i> 55 2504 (1982)
RX (1°RI , allyl or benzyl Br), $\text{KF} \cdot \text{Celite}$	<i>CL</i> 45 (1979)
RX ($\text{R} = 1^\circ, 2^\circ$ alkyl; benzylic), $\text{Et}_4\text{NF}, \text{DMF}$	<i>Can J Chem</i> 57 1887 (1979)
RX ($\text{R} = 1^\circ, 2^\circ$ alkyl; allylic; benzylic), NaOH , ($\text{PhCH}_2\text{NEt}_3$)Br, $\text{H}_2\text{O}, \text{CH}_2\text{Cl}_2$	<i>Tetr</i> 30 1379 (1974)
RX ($\text{R} = 1^\circ, 2^\circ$ alkyl; allylic; benzylic), anion exchange resin	<i>Syn</i> 113 (1977)
RX (3°RCl), cat $\text{Ni}(\text{acac})_2, \text{NaHCO}_3$	<i>Syn</i> 186 (1982)
RX ($1^\circ \text{RI}, \text{ArCH}_2\text{Br}, \text{RCOCH}_2\text{I}$), Ag_2O	<i>JACS</i> 110 301 (1988)
$\text{R}_2\text{CHOMs}, \text{CsF}$	<i>SL</i> 336 (1995)

allylic carboxylate, base, Pd catalyst (R = allylic)	JOC 54 2759 (1989)
allylic carbonate, cat Pd ₂ (DBA) ₃ , cat dppb (R = allylic)	SL 725 (1992)
HC≡CCMe ₂ X (X = Cl, O ₂ CCF ₃ , OCO ₂ Me); cat CuCl or CuCl ₂ ; DBU	TL 35 6405 (1994)
(Me ₃ O)BF ₄	J Prakt Chem 867 (1964)
Me ₂ S ⁺ OCH ₂ ⁻ (R = Me)	TL 867 (1964)
(Me ₃ S)I, Ag ₂ O	Ann 611 117 (1958)
Me ₃ SOH	JOC 44 638 (1979)
Me ₃ SeOH	TL 1787 (1979)
ROH (R = 1°, 2°, 3° alkyl), R'O ₂ CN=NCO ₂ R', PPh ₃	JCS Perkin I 461 (1975) Chem Ind 281 (1975) TL 2243 (1978); 29 1389 (1988); 30 2297 (1989); 31 2201 (1990); 34 1195 (1993); 36 6193 (1995) (on polymer) Heterocycles 20 1975 (1983) JOC 50 3095 (1985); 53 4081 (1988); 59 3442 (1994)
ROH (R = 2° allylic), EtO ₂ CN=NCO ₂ Et, n-Bu ₃ P	JACS 107 3891 (1985)
CH ₂ N ₂	JOC 53 4724 (1988)
CH ₂ N ₂ , cat HBF ₄	JACS 80 2584 (1958) Tetr 6 36 (1959) Org Syn Coll Vol 5 245 (1973)
Ph ₄ BiO ₂ CCF ₃ (R = Ph)	CC 503 (1981)
Ph ₃ Bi(OAc) ₂ , cat Cu or Cu(OAc) ₂ (R = Ph)	J Gen Chem USSR 55 2232 (1985) TL 27 3619 (1986)



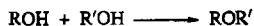
TL 32 6315 (1991)



Reagent

R

H ₃ PO ₄	benzhydryl	JACS 73 2630 (1951)
ZnCl ₂	2° allylic; 1° or 2° benzylic	JOC 52 3917 (1987)
CuSO ₄ , 180°C	1° alkyl	Acta Chem Scand B 31 721 (1977)
DMSO, 175°C	1° or 2° benzylic	JOC 42 2012 (1977)

ReagentR H^+ $2^\circ, 3^\circ \text{R}; \text{Ar}_3\text{C}; \text{Ar}_2\text{CH}$

IACS 54 2088 (1932); 70

2400 (1948)

Org Syn Coll Vol 4 72 (1963)

DMSO, 175°C

benzylic

JOC 42 2012 (1977)

 $\text{Mg}(\text{ClO}_4)_2$

allylic, benzylic

TL 36 2679 (1995)

 ZnCl_2

allylic, benzylic

JOC 52 3917 (1987)

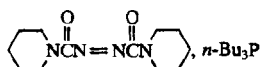
cat I_2 3°R

TL 29 2445 (1988)

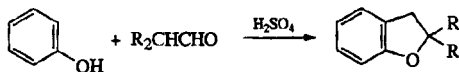
 I_2

benzylic

Can J Chem 44 2337 (1966)

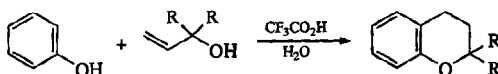
 $1^\circ, 2^\circ \text{R}; \text{allylic}; \text{benzylic}$

TL 35 5997 (1994)

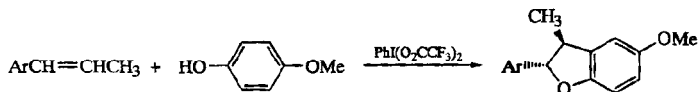


JOC 35 2904 (1970)

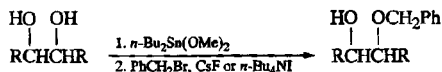
TL 34 7829 (1993)



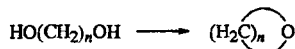
TL 33 3795 (1992)



JOC 56 1979 (1991)



SL 913 (1993)

Reagent(s)nDMSO, Δ


4, 5

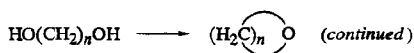
JOC 28 1388 (1963); 29 123 (1964)

 $\text{CF}_3\text{CO}_2\text{H}$

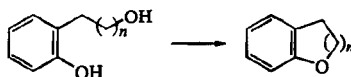
4

TL 29 6211 (1988)

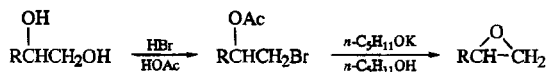
TsOH	4	Org Syn Coll Vol 4 534 (1963) JOC 37 1947 (1972); 54 5657 (1989) JACS 113 5072 (1991)
HCl	5	JOC 58 898 (1993)
HBF ₄	6-9	TL 36 3549 (1995)
Nafion-H	4-7	Syn 474 (1981)
Amberlyst 15	5	Syn 208 (1973)
various Brønsted and Lewis acids	4	Tetr 37 2149 (1981)
BF ₃ ·OEt ₂	4, 6-9	JOC 59 5999 (1994) TL 36 3549 (1995)
Al ₂ O ₃	4-6	BCSJ 53 3031 (1980)
ZnCl ₂	4, 5, 11	JOC 52 3917 (1987)
(CH ₃) ₂ C(OAc)COBr/NaOMe	2	TL 30 6257 (1989) JACS 112 8907 (1990)
(CH ₃) ₂ C(OAc)COBr/Amberlite IRA-400, CH ₃ OH	2	TL 24 367 (1984); 28 4959 (1987); 36 6991 (1995)
(CH ₃) ₂ C(OAc)COBr/BioRad AG-1-X8 (OH ⁻), MeOH	2	JACS 110 7217 (1988)
Me ₂ SO ₄	4	JACS 103 7398 (1981)
<i>n</i> -BuLi/TsCl/ <i>n</i> -BuLi	3	Syn 550 (1981)
NaH/TsN ₂ 	2	JACS 110 854 (1988)
TsCl, py	2, 4, 5	JACS 72 1593 (1950) TL 2731 (1975); 36 1723 (1995) JOC 45 1828 (1980)
Me ₃ SiCl, py/Tf ₂ O/HOCH ₂ CH ₂ OH	3	JOC 57 3274 (1992)
Tf ₂ O, py	2, 4	JOC 58 1762 (1993) TL 36 47 (1995)
Ph ₂ S[OC(CF ₃) ₂ Ph] ₂	2, 4, 5	JACS 96 4604 (1974); 112 8985 (1990) Helv 61 822 (1978)
(Me ₂ N ⁺ =CCl ₂)Cl ⁻ /NaOMe or MeLi	2	TL 27 4697 (1986) (from cis diols)
[(CH ₃) ₃ CN=C=N(CH ₃)-C(CH ₃) ₃]BF ₄ /Et ₃ N, Δ	4-6	JACS 97 464 (1975)
EtO ₂ CN=NCO ₂ Et, P(OMe) ₃	3	JACS 112 3535 (1990)
EtO ₂ CN=NCO ₂ Et, PPh ₃	2-6	BCSJ 49 510 (1976) TL 5153 (1978); 30 6797 (1989); 36 47, 3019 (1995) JOC 48 5396 (1983); 53 2598 (1988) JACS 116 2340 (1994)



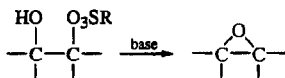
Reagent(s)	<i>n</i>	
(MeO) ₂ CHNMe ₂	2	JACS 95 242 (1973); 97 3468 (1975) Org Syn Coll Vol 6 887 (1988)
NBS, PPh ₃	4	TL 34 2981 (1993)
CCl ₄ , PPh ₃ , (K ₂ CO ₃)	2, 4, 5	JOC 46 3361 (1981); 47 3980 (1982); 48 5396 (1983) TL 24 661 (1983)
CCl ₄ , P(NMe ₂) ₃ / (NaOR)	2, 3	TL 4459 (1973); 3459 (1975) Tetr 32 1283 (1976)
P(OEt) ₅	4	JACS 93 4004 (1971)
Ph ₃ PO, (CF ₃ SO ₂) ₂ O	2, 4	SL 423 (1990)
Ph ₃ P(OEt) ₂	2, 4, 5	Phosphorus 1 151 (1971) JACS 93 4004 (1971); 107 5210 (1985) JOC 48 5396 (1983); 52 525 (1987) (1,4-oxathianes) Phosphorus and Sulfur 26 15 (1986)
Ph ₃ P(OCH ₂ CMe ₃) ₂	2, 4, 5	JOC 51 5490 (1986)
polymer-PPh ₂ (OEt) ₂	2, 4, 5	JOC 50 5007 (1985)



Reagents	<i>n</i>	
EtO ₂ CN=NCO ₂ Et, PPh ₃	1-3	TL 25 3955 (1984); 26 123 (1985); 34 7483 (1993) Chem Pharm Bull 35 1930 (1987) JOC 52 2029 (1987); 59 4346 (1994)
CCl ₄ , PPh ₃ , Et ₃ N	2	TL 34 7483 (1993)
(COCl) ₂ , DMF/Et ₃ N	1, 2	TL 34 7483 (1993) JOC 59 4346 (1994)



JCS Perkin I 1214 (1973)
Tetr 33 289 (1977)
Org Syn Coll Vol 7 356 (1990)



R = Me, *p*-Tol

Helv 30 1929 (1947)

Angew Int 18 958 (1979)

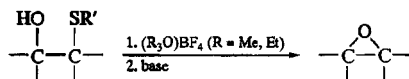
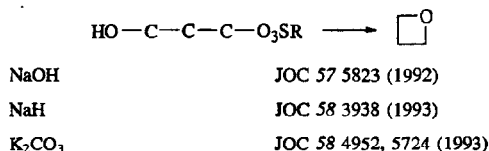
JACS 102 7984 (1980); 109 6205 (1987); 112 6942 (1990)

TL 24 4539 (1983); 28 2619, 2627, 2863, 6191 (1987); 29 865 (1988); 30 2751, 7165 (1989); 31 1003 (1990);

32 363 (1991); 33 2095 (1992); 34 3033 (1993); 35 7197 (1994)

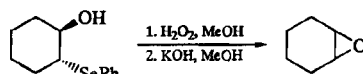
JOC 50 5687 (1985); 52 2378 (1987); 55 1957 (1990); 56 2869, 6759 (1991); 57 5818 (1992); 58 385 (1993)

SL 551 (1991); 266 (1992); 745 (1994); 613 (1995)

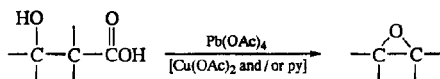


JOC 50 5687 (1985); 59 533 (1994)

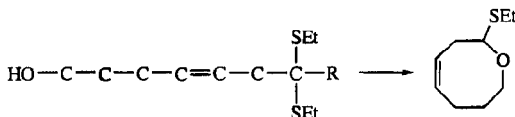
TL 27 6329 (1986); 28 797, 5677 (1987); 31 2895 (1990); 33 931 (1992)



TL 36 5079 (1995)



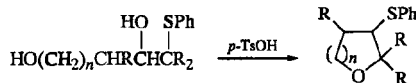
JOC 55 1967 (1990)


 NCS, AgNO₃, 2,6-lutidine, silica gel,
molecular sieves

JACS 111 5321 (1989)

 AgClO₄, NaHCO₃ or pyridine

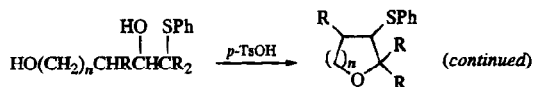
JACS 111 5321 (1989)


 $\frac{n}{1}$

1

 TL 27 101 (1986); 28 1925 (1987); 29 4885, 5321
(1988); 31 3457 (1990); 32 5409, 6645 (1991); 33
539, 4369 (1992); 34 6783 (1993)

JCS Perkin I 451 (1991)

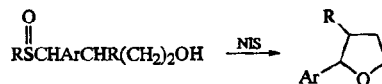
 n

1, 2

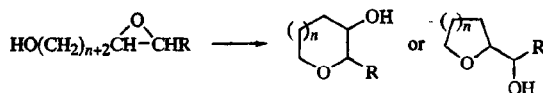
TL 36 1723 (1995)

2

TL 32 3425, 5409 (1991); 33 539 (1992); 36 1909 (1995)



TL 33 965 (1992)

ReagentRing Size H^+

5

JACS 112 5276 (1990)
JOC 57 115 (1992); 60 1170 (1995)
TL 35 7629 (1994)

5, 6

JACS 111 5330 (1989)
TL 36 8771 (1995)

6

TL 29 3171 (1988); 35 5023 (1994)
JACS 111 5321, 6666, 6676, 6682 (1989);
114 7935 (1992); 115 3558 (1993); 117
10227, 10252 (1995)

6, 7

JOC 57 50 (1992); 60 5843 (1995)
JACS 111 5335 (1989) SnCl_2

7

JCS Perkin I 1589 (1985)
TL 29 2867 (1988) $n\text{-Bu}_3\text{SnOMe}$

4, 5

TL 2249 (1976)

cat $\text{Ln}(\text{OTf})_3$

5, 6

TL 36 8063 (1995)

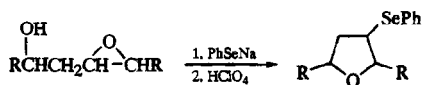
 $\text{KCH}_2\text{SOCH}_3$

7

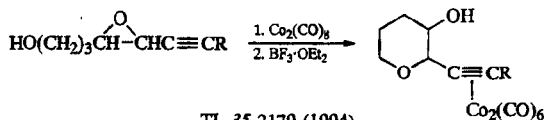
JOC 59 715 (1994)

KOH

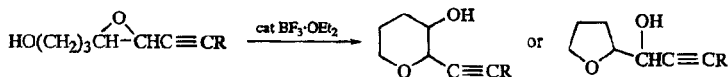
4, 5

CC 864 (1976)
BCSJ 50 1226 (1977)
TL 371 (1978)
Tetr 46 7703 (1990)

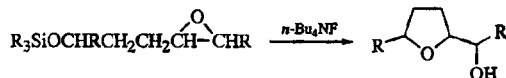
JACS 112 8995 (1990)



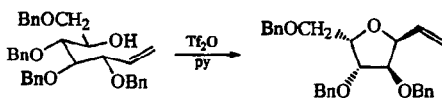
TL 35 2179 (1994)



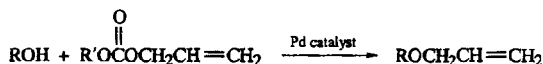
TL 35 2183 (1994)



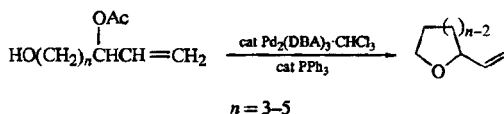
TL 35 319 (1994)



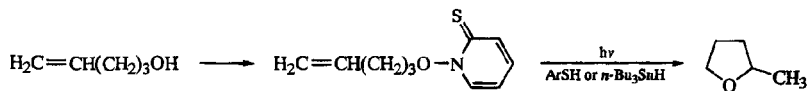
TL 36 47, 2831 (1995)



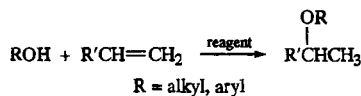
TL 30 4669 (1989); 35 2357 (1994)


 $n = 3-5$

TL 29 2927 (1988)



JOC 60 6706 (1995)



Reagent

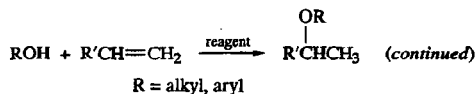
 H^+

Ind Eng Chem 43 1596 (1951)

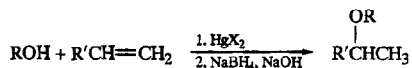
 JOC 20 1232 (1955); 21 247 (1956); 44 1438 (1979);
56 3447 (1991)

Proc Chem Soc 249 (1961)

Rec Trav Chim 81 691 (1962)

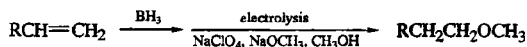
Reagent

	JCS 755 (1963)
	TL 36 1483 (1995) (intramolecular)
Amberlyst H-15	TL 29 2951 (1988)
cat $\text{BF}_3 \cdot \text{OEt}_2$	Org Syn Coll Vol 8 204 (1993)
	TL 34 5893 (1993)
cat $\text{BF}_3 \cdot \text{OEt}_2$, cat H_3PO_4	Org Syn Coll Vol 7 66 (1988)

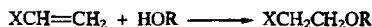


X = OAc, O_2CCF_3 , ClO_4 , NO_3 , BF_4

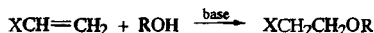
TL 5165 (1967); 33 4863 (1992) [$\text{Hg}(\text{BF}_4)_2$, diene regioselectivity]; 35 5182 (1994) (intramolecular); 36 463 (1995) (intramolecular)
 JACS 91 5646 (1969); 105 7407 (1983)
 R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 3 (review)
 JOC 55 863 (1990); 57 2888 (1992); 58 291 (1993); 59 2219 (1994) (all intramolecular)



CL 1021 (1974)

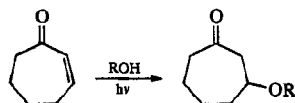
XReagent

Ar	$h\nu$	JOC 54 1354 (1989)
COR	H_2SO_4	JOC 17 962 (1952)
CO_2R	ZnBr_2	TL 5895 (1993) (intramolecular)

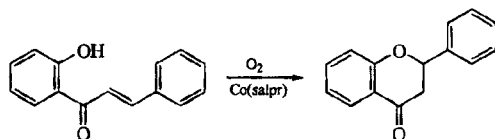
X

COR	JACS 100 5141 (1978); 116 3324 (1994)
	JOC 44 2722 (1979); 55 3562 (1990)
	TL 30 6653 (1989); 35 323 (1994) (both intramolecular)
CO_2R	JACS 68 544 (1946); 72 2205 (1950); 112 3665 (1990)
	JCS 2035 (1949)
	Acta Chem Scand B 31 297 (1977)

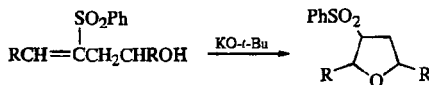
	TL 29 1255 (1988); 31 763 (1990) (intramolecular); 33 2399 (1992) (intramolecular); 34 5467, 5471, 5739 (1993) (all intramolecular); 35 703, 7401 (1994) (both intramolecular) JOC 55 3562 (1988); 58 6177 (1993) (intramolec- ular); 60 6688 (1995) (intramolecular)
CN	JCS 535 (1945) SL 53 (1992)
NO ₂	JOC 55 5900 (1990) TL 34 1259 (1993)
SO ₂ Ph	TL 26 4455 (1985); 33 695 (1992) (both intramo- lecular)



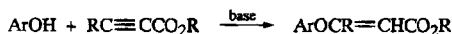
TL 257 (1964); 2025, 3635, 5075, 5443 (1968)
 JACS 88 2602 (1966); 89 3949 (1967); 90 6251 (1968); 92 4656 (1970); 100 5141 (1978)
 BCSJ 40 945 (1967); 47 1460 (1974)
 CC 1695 (1970)
 Can J Chem 51 2215 (1973)
 JOC 44 2722 (1979)



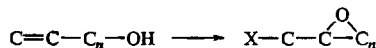
TL 30 4145 (1989)



TL 36 7531 (1995)





See page 418, Section 2.4.

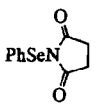
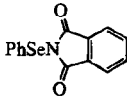
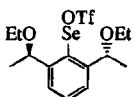


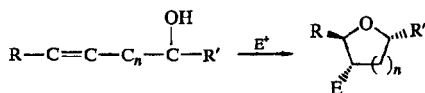
Review: P. A. Bartlett, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York
 (1984), Vol 3, Part B, Chpt 6

For intermolecular reactions, see page 638, Section 4.

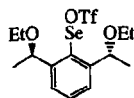
<u>X</u>	<u>Reagent(s)</u>	
Br	Br ₂	JOC 52 4191 (1987)
	CH ₃ CONHBr	JOC 55 5580 (1990)
	NBS	CC 264 (1969)
		JACS 93 5813 (1971); 101 260 (1979); 106 2668 (1984); 111 3728 (1989); 114 5018 (1992)
		JOC 52 1686, 4191 (1987); 53 640, 5876, 5885 (1988); 54 346 (1989); 55 891, 2752 (1990); 57 5670 (1992)
		TL 28 3065 (1987)
		SL 523 (1990)
	NBS, cat Br ₂	JOC 57 915 (1992)
	2,4,4,6-tetrabromo-2,5-cyclohexadienone	CL 1187 (1976)
		JACS 106 2668 (1984); 112 2749 (1990)
I		TL 29 3149, 3171 (1988)
		JOC 55 5088 (1990); 56 1347 (1991)
	I ₂	JOC 51 2230 (1986); 54 346 (1989)
	I ₂ , NaHCO ₃	JACS 103 3963 (1981); 107 3271 (1985); 110 4533 (1988); 111 2204, 3712 (1989)
		TL 26 2885 (1985); 29 2011 (1988); 33 6507, 6511 (1992); 35 6611, 7259 (1994); 36 1787, 8179 (1995)
		JOC 52 4062, 4191, 4449 (1987); 53 2548 (1988); 56 2476, 4238 (1991); 59 1166, 6643 (1994)
		SL 523 (1990); 40 (1994); 663 (1995)
	I ₂ , K ₂ CO ₃	JOC 60 3311 (1995)
	I ₂ , KI	Proc Acad Sci USSR, Chem Sec 146 787 (1962)
		JOC 55 5580 (1990)
	I ₂ , KI, NaHCO ₃	BCSJ 53 3383 (1980)
	I ₂ , py	TL 36 8179 (1995)
	I ₂ , 	TL 36 8179 (1995)
	I ₂ , Bi(OAc) ₃	JOC 55 5580 (1990)
	I ₂ , PhI(OAc) ₂	TL 32 7493 (1991); 33 4687 (1992)
	I ₂ , CuCl ₂	JOC 55 5580 (1990)
	I ₂ , AgO ₂ CCF ₃	JACS 114 1084 (1992)
		SL 663 (1995)
	I ₂ , TiO ₂ CCF ₃	JOC 55 5580 (1990)
	I ₂ , TiClO ₄	JOC 55 5580 (1990)
	I ₂ , HgO	JOC 57 1966 (1992)
	I ₂ , HgO, hν	TL 28 4011 (1987)
	I ₂ , CAN	JOC 55 5580 (1990)
	NIS	JOC 51 2230 (1986); 57 5670 (1992)
		JACS 110 1985 (1988); 112 5583 (1990)
		TL 34 8435 (1993)
	iodonium dicollidine perchlorate	JOC 52 4062 (1987)
	iodonium dicollidine hexafluorophosphate	SL 323 (1995)

OH	<i>m</i> -ClC ₆ H ₄ CO ₂ H	TL 28 5501 (1987)
	<i>t</i> -BuO ₂ H, cat VO(acac) ₂ /HOAc	TL 2741 (1978); 28 5501, 5665 (1987); 29 5947 (1988)
		JOC 56 2299 (1991)
		JACS 116 7921 (1994)
	H ₂ O, Ti(O ₂ CCF ₃) ₃ , HBF ₄	JOC 50 2416 (1985)
	CrO ₃ ·2py	TL 23 727 (1982)
	PCC	TL 23 727 (1982); 29 3171 (1988)
		JACS 116 7921 (1994)
	Re ₂ O ₇	TL 33 3729, 5299 (1992)
		JACS 117 1447 (1995)
	cat Re ₂ O ₇ , <i>t</i> -BuO ₂ H	TL 33 5303 (1992)
	ReO ₃ , H ₃ IO ₆	TL 33 5303 (1992)
		JACS 117 1447 (1995)
OR	(CF ₃ CO ₂)ReO ₃	JOC 60 5750 (1995)
	(Cl ₂ CHCO ₂)ReO ₃ , (Cl ₂ CHCO) ₂ O	JOC 60 5750 (1995)
	2,4,4,6-tetrabromo-2,5-cyclohexa-dienone/AgBF ₄ , MeOH	JACS 106 2668 (1984)
	I ₂ , AgO ₂ CCF ₃ , H ₂ O	JOC 55 5580 (1990)
	I ₂ , HIO ₄	JOC 55 5580 (1990)
	TLX ₃ (X = NO ₃ , O ₂ CCF ₃), MeOH	JOC 50 2416 (1985)
	AgO ₂ CCF ₃ , MeOH	JOC 55 5580 (1990)
ONO ₂	Ti(NO ₃) ₃	JOC 50 2416 (1985)
SMe	MeSCl, <i>i</i> -Pr ₂ NEt	TL 28 523 (1987)
	(MeSSMe ₂)BF ₄ , <i>i</i> -Pr ₂ NEt	TL 26 6159 (1985)
	(MeSSMe ₂)SbCl ₆	JCS Perkin I 3106 (1981)
SAr	<i>n</i> -BuLi/PhSCl	TL 28 523 (1987)
	PhSCl, <i>i</i> -Pr ₂ NEt	TL 28 523 (1987)
	PhSN  O, CF ₃ SO ₃ H	CC 1280 (1987)
		TL 32 2261 (1991)
	ArSSCN, LiClO ₄ (Ar = Ph, <i>p</i> -Tol)	JOC USSR 14 2265 (1978)
	(ArS) ₂ , (NH ₄) ₂ S ₂ O ₈ , CF ₃ SO ₃ H	JOC 57 4025 (1992)
Ts	TsI / base	TL 33 1779 (1992)
SePh	(PhSe) ₂ , electrolysis	TL 28 4343 (1987)
	(PhSe) ₂ , hv	JOC 57 4019 (1992)
	PhSeCl	CC 725 (1977)
		TL 1257 (1977); 21 129 (1980) (allenlic alcohols); 31 5917 (1990); 34 8435 (1993)
		Can J Chem 55 3894 (1977)
		JACS 102 3784 (1980); 106 3353 (1984); 109 2082 (1987); 114 1084, 7318 (1992)
		Tetr 37 4097 (1981) (review)
		JOC 51 495 (1986); 52 4191 (1987); 54 346 (1989); 55 5580 (1990); 57 5670 (1992)
		SL 269 (1992)
	PhSeCl, TiO ₂ CCF ₃	JOC 55 5580 (1990)
	PhSeBr	Helv 61 3075 (1978)
		JOC 55 5580 (1990)

<u>X</u>	<u>Reagent(s)</u>	
	PhSeO ₂ CCF ₃ PhSeOTf PhSeOTs	TL 33 1949 (1992) TL 28 4297, 4415 (1987); 31 5917 (1990) JOC 56 2781 (1991)
		Tetr 37 4097 (1981) (review)
		Tetr 37 4097 (1981) (review) JACS 107 7792 (1985); 114 7318 (1992) JOC 52 4191 (1987); 57 5670 (1992); 60 1435 (1995) SL 279 (1990)
SeAr		JOC 60 4660 (1995)
TeAr	(ArTeO) ₂ O / NH ₂ NH ₂ (ArTeO)OAc / NH ₂ NH ₂	TL 28 1281 (1987) JOC 54 4391 (1989) JOC 54 4391 (1989)
TeX ₂ Ar	ArTeX ₃ (X = Cl, Br)	TL 28 5611 (1987)
NHAc	TI(O ₂ CCF ₃) ₃ , CH ₃ CN	JOC 50 2416 (1990)
HgX	HgX ₂ (X = OAc, O ₂ CCF ₃)	R. C. Larock, "Solvomercuration / Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 3 (review) JOC 52 4191 (1987); 53 4181, 5873 (1988); 54 346 (1989); 55 5580 (1990); 59 2219 (1994) TL 32 4831 (1991); 34 8435 (1993) SL 525 (1993)

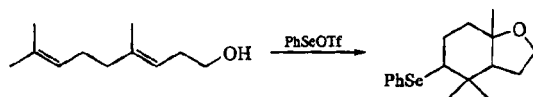


<u>E⁺</u>	<u>n</u>	
I ₂ , K ₂ CO ₃	1	TL 34 1955 (1993)
PhSeCl	1	TL 32 4015 (1991); 36 2987 (1995) SL 1191 (1995)
PhSeCl, Lewis acid	1	TL 31 5917 (1990); 34 1955 (1993)
2,4,6-(<i>i</i> -Pr) ₃ C ₆ H ₂ SeBr	1	JOC 60 3572 (1995)
PhSeOTf	1	TL 31 5917 (1990)

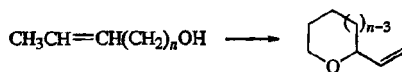


1, 2

JOC 60 4660 (1995)



TL 31 6535 (1990)


 $n = 3, 4$

 Pd(OAc)₂, DMSO

TL 30 4925 (1989)

Pure Appl Chem 62 2035 (1990)

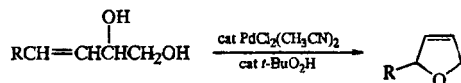
 O₂, cat Pd(OAc)₂, Cu(OAc)₂

TL 1821 (1976)

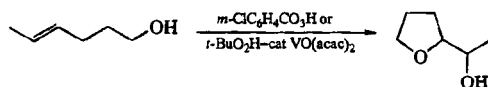
JOC 57 6083 (1992)

 O₂, cat Pd(OAc)₂, DMSO

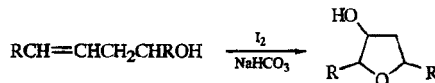
TL 36 7749 (1995)



SL 237 (1992)

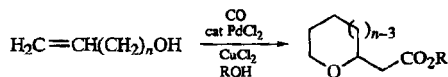


TL 35 6453 (1994)



TL 33 6507 (1992)

SL 295 (1994)

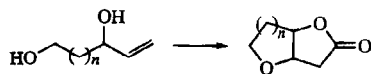

 $n = 3, 4$

JACS 104 5850 (1982); 105 2034 (1983); 106 1496 (1984); 116 7455 (1994)

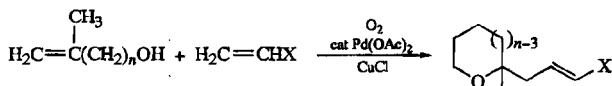
JOC 47 4382 (1982); 54 98, 4483, 4485 (1989); 55 5580 (1990)

TL 25 3171 (1984)

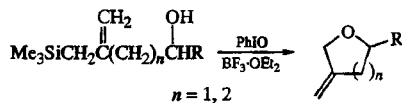
Pure Appl Chem 62 2035 (1990)

 n Reagent

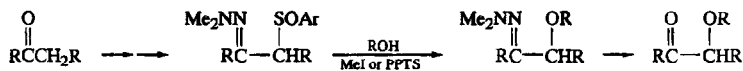
- | | | |
|---|---|------------------------------------|
| 1 | CO, cat PdCl ₂ , CuCl ₂ , NaOAc, HOAc | TL 26 3207 (1985)
SL 191 (1992) |
| 2 | CO, Pd(OAc) ₂ | TL 25 3171 (1984) |

 $n = 3, 4$; X = Ar, COR, CO₂R

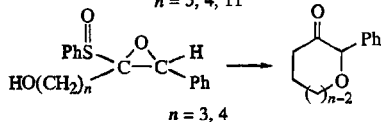
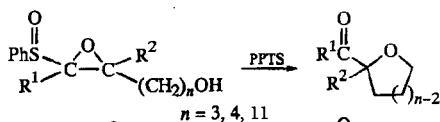
TL 34 7205 (1993)



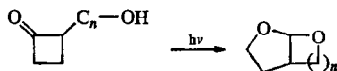
CC 1108 (1982)



TL 30 2791 (1989)



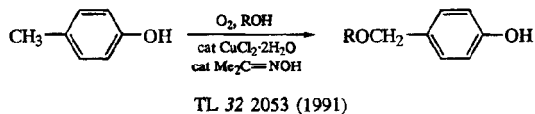
TL 28 2603 (1987)

 $n = 2, 3$

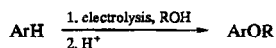
JACS 111 5824 (1989)

3. ALKANE, ARENE, ALKENE AND ALKYNE ADDITIONS AND SUBSTITUTIONS

1. Alkane Substitution



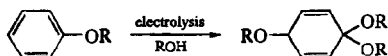
2. Arene Addition and Substitution



JACS 103 2361 (1981)

S. Torii, "Electroorganic Synthesis: Methods and Applications, Part 1: Oxidations," Monographs in Modern Chemistry, Vol 15, Kodansha, Tokyo, and VCH, Weinheim (1985)

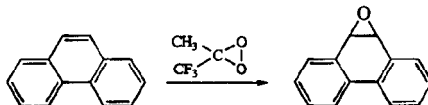
TL 30 4037 (1989)



JCS Perkin I 708 (1978)

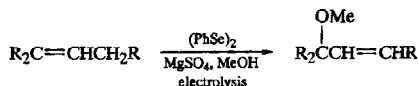
JACS 103 2361 (1981)

TL 30 4037 (1989); 31 1513 (1990)

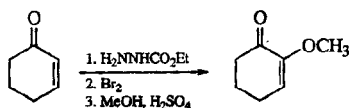


TL 31 6097 (1990)

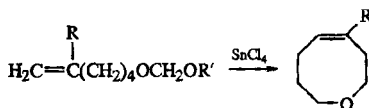
3. Alkene Substitution



JACS 103 4606 (1981)



JOC 59 6026 (1994)



See page 931, Section 1.

4. Alkene Addition

See also page 889, Section 2.



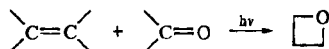
electrolysis, MeOH

TL 30 4037 (1989)

(PhIOiPh)X (X = BF₄, SbF₆, PF₆), MeOH

TL 29 3717 (1988)

JOC 54 2609 (1989)



Reviews:

Adv Photochem 6 301 (1968)

Org Photochem 5 1 (1981)

H. A. J. Carless, "Synthesis Organic Photochemistry," Ed. W. M. Horspool, Plenum Press, New York (1984), p 425

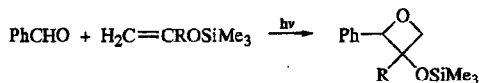
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 2.4, p 151

Gazz Chim Ital 39 341 (1909)

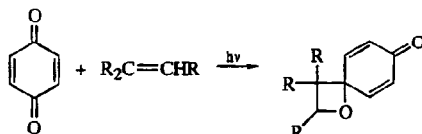
JACS 76 4327 (1954); 94 1776 (1972) (intramolecular); 106 4186, 7200 (1984); 111 5367 (1989); 112 1202, 1281 (1990); 113 6923 (1991)

TL 3657 (1964); 79 (1969) (intramolecular); 24 3217 (1983); 28 5933, 6151 (1987) (both intramolecular); 29 6689 (1988) (furan); 31 5445 (1990) (furan); 36 19, 6851 (intramolecular) (1995)

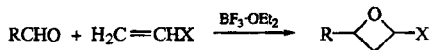
JOC 34 3579 (1969) (intramolecular); 39 1850 (1974) (intramolecular); 41 1229 (1976) (intramolecular); 45 1286 (1980) (intramolecular); 56 5020 (1991); 59 1027 (intramolecular), 4677 (1994)
 BCSJ 48 1907 (1975) (intramolecular)
 CC 667 (1984)
 Ber 118 1485 (1985); 120 307 (1987)
 Science 227 857 (1985)
 Angew Int 24 877 (1985)



TL 32 7037 (1991); 35 5845 (1994)

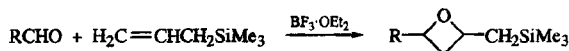


TL 34 3505 (1993)

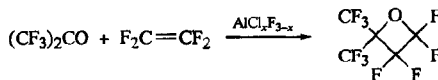


X = OR, SR

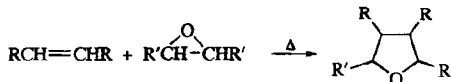
TL 30 1571 (1989)



TL 29 4953 (1988)

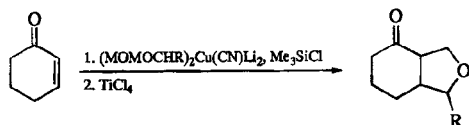


JOC 60 3419 (1995)

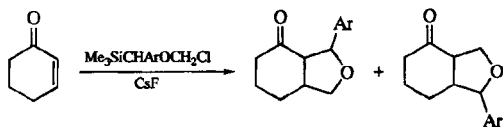


Review: Angew Int 16 572 (1977)

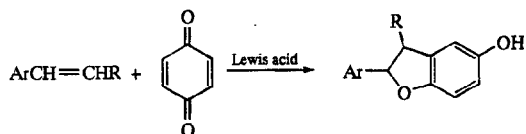
JACS 87 3657, 3665 (1965)
 CC 1190, 1192 (1971); 134 (1984)
 JOC 41 2654 (1976); 43 4256 (1978)
 TL 21 4909 (1980) (intramolecular); 23 4665 (1982) (intramolecular); 25 1137 (1984) (intramolecular); 28 3155 (1987)
 Ber 117 2157 (1984)



JACS 110 6249 (1988)



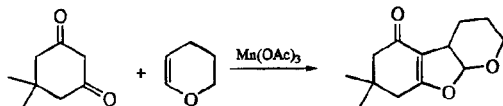
TL 34 5943 (1993)



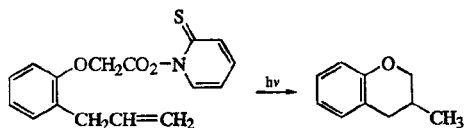
JACS 110 7931 (1988); 113 5068 (1991) (chiral)

TL 35 1661 (1994)

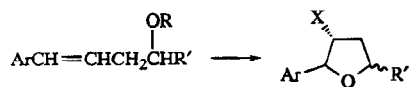
JOC 59 6567, 6588 (1994)



TL 32 7107, 7111 (1991)



TL 30 4731 (1989)

R = CH₂OMe, CHMeOEt, SiR₃X

I

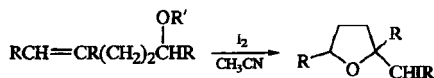
PhSe

ReagentI₂

PhSeCl

TL 34 7579 (1993)

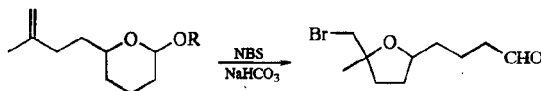
TL 32 4015 (1991)



JACS 103 3963 (1981)

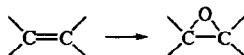
TL 27 2195 (1986); 29 2011 (1988); 33 1747 (1992)

IOC 52 320, 5067 (1987)



CC 1462 (1987)

5. Epoxidation of Alkenes



Reviews:

Org Rxs 7 378 (1953) (peracids); 48 1 (1996) (Katsuki-Sharpless oxidation)

Topics Stereochem 7 93 (1973) (stereochemistry)

Chem Rev 89 431 (1989) (transition metal catalyzed); 92 873 (1992) (metal-mediated)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Parts 3.1 and 3.2, pp 357-436

Russ Chem Rev 60 123 (1991) (enantioselective)

"Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 4 (asymmetric epoxidation of allylic alcohols and unfunctionalized alkenes)

Topics Curr Chem 164 1, 45 (dioxiranes), 63 (enantioselective) (1993)

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21e, G. Thieme, Stuttgart-New York (1995), p 4599 (enantioselective)

Pseudomonas oleovorans monooxygenase
(enantioselective)

IOC 46 3129 (1981)

JACS 113 5878 (1991) (allylic ethers)

Nocardia corallina (enantioselective)

TL 30 1583 (1989)

Aspergillus niger (enantioselective)

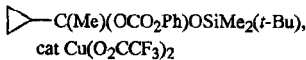

TL 33 5241 (1992)

chloroperoxidase (enantioselective)

JACS 117 10419 (1995)

m-ClC₆H₄CO₃HTL 849 (1965); 4347, 4733 (1979); 26 4895 (1985); 29 2475 (1988) (allylic and homoallylic *O*-carbamates); 30 1309 (4-alkenoic acids), 1427 (in H₂O), 1913, 2775, 3935 (1989); 31 1055 (1990); 32 1671, 6355 (allylic fluorides), 6943, 7123 (1991); 33 1447, 1879, 5503 (1992); 34 611, 1327, 2119, 7187 (1993); 35 4939, 6155 (1994)

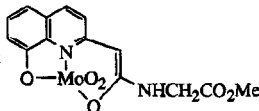
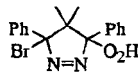
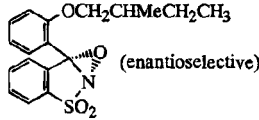
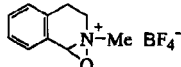
IOC 32 1363 (1967); 35 251 (1970); 36 3832 (1970); 38 1380 (allylic alcohols), 1385 (1973); 50 2179 (1985); 51 2505 (1986); 52 4495, 4511 (1987); 53 2180, 2398 (1988); 55 3236 (1990); 57 6025 (1992); 58 5221, 7929 (1993); 59 1139, 2204 (1994); 60 1026, 3692, 6214 (1995)


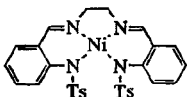
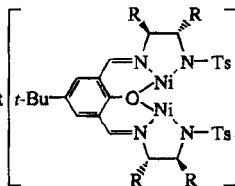
- JCS C 731 (1970)
 JACS 92 6914 (1970); 96 5254 (1974); 106 7854 (1984); 109 5437, 7838 (1987); 110 2978 (1988) (allylic alcohols); 111 6861 (1989); 114 3044 (1992); 115 7653 (1993)
 CC 421 (1976)
 JCS Perkin I 2885 (1982)
- m*-ClC₆H₄CO₃H, NaHCO₃ JOC 38 2267 (1973); 57 1198 (1992)
 TL 427 (1977)
- m*-ClC₆H₄CO₃H, Na₂CO₃ JOC 52 4647 (1987)
 TL 32 1671 (1991)
- m*-ClC₆H₄CO₃H, K₂CO₃ or K₂HPO₄ JOC 43 610 (1978)
- m*-ClC₆H₄CO₃H, phosphate JOC 43 610 (1978); 44 1351 (1979); 58 7180 (1993)
- m*-ClC₆H₄CO₃H, KF TL 22 3895 (1981); 35 8433 (1994)
- m*-ClC₆H₄CO₃H, NMO, cat chiral Mn(salen) (enantioselective) JACS 116 9333 (1994)
 TL 36 5457 (1995)
 JOC 60 5380 (1995)
- 3,5-(NO₂)₂C₆H₃CO₃H JOC 43 3163 (1978); 55 4668 (1990)
 JACS 106 7854 (1984)
 TL 28 2771 (1987)
- 3,5-(NO₂)₂C₆H₃CO₃H, Na₂HPO₄ JACS 109 5167, 5280 (1987)
- o*-HO₂CC₆H₄CO₃H JACS 82 6373 (1960)
- o*-HO₂CC₆H₄CO₃H, base SL 475 (1991)
 JOC 57 1198 (1992)
- CH₃CO₃H TL 33 753 (1992)
- CH₃CO₃H, NaOAc JCS Perkin I 2909 (1982)
 JOC 57 86 (1992)
- CH₃CO₃H, Na₂CO₃ JACS 82 4328 (1960)
- CH₃CO₃H, cat Mn porphyrins TL 36 2317 (1995)
- CF₃CO₃H JACS 106 7854 (1984); 115 444 (1993)
 TL 26 4895 (1985)
- PhCH₂OCO₃H JOC 39 3054 (1974)
- magnesium monoperoxyphthalate Syn 1015 (1987)
 TL 36 837 (1995)
- magnesium monoperoxyphthalate, cat Mn porphyrin TL 36 837 (1995)
-  C(Me)(OCO₂Ph)OSiMe₂(*t*-Bu),
 cat Cu(O₂CCF₃)₂ TL 28 1909 (1987)
- H₂O₂, ArSO₂N₂, NaOH, CH₃CN SL 915 (1993)

H ₂ O ₂ , ArSeO ₂ H	JOC 42 2035 (1977) Syn 299 (1978)
H ₂ O ₂ , cat H ₃ PMo ₁₂ O ₄₀ , cat [C ₅ H ₅ N(CH ₂) ₁₅ CH ₃]Cl	JOC 53 3587 (1988)
H ₂ O ₂ , cat [C ₅ H ₅ N(CH ₂) ₁₅ CH ₃] ₃ PMo ₁₂ O ₄₀ (allylic alcohols)	Syn Commun 14 865 (1984)
H ₂ O ₂ , [C ₅ H ₅ N(CH ₂) ₁₅ CH ₃] ₃ PMo ₁₂ O ₄₀	JOC 52 1868 (1987)
H ₂ O ₂ , cat tungstic acid, Et ₃ N (allylic alcohols)	JACS 87 734 (1965)
H ₂ O ₂ , cat tungstic acid, NaOAc or Me ₃ NO	TL 27 707, 711 (1986)
H ₂ O ₂ , cat Na ₂ WO ₄ ·2H ₂ O, H ₃ PO ₄ , H ₂ SO ₄ , phase transfer catalyst	JOC 48 3831 (1983)
H ₂ O ₂ ; [(<i>n</i> -C ₈ H ₁₇) ₂ NCH ₃]HWO ₄ or [(<i>n</i> -C ₈ H ₁₇) ₃ NCH ₃] ₂ WO ₄ ; (<i>n</i> -C ₈ H ₁₇) ₃ PO, PhPO ₃ H ₂ or C ₁₂ H ₂₅ PO ₃ H ₂	TL 28 2237 (1987)
H ₂ O ₂ , cat (PhCH ₂ PPh ₃) ₂ W ₂ O ₁₁	TL 27 2617 (1986)
H ₂ O ₂ , cat (<i>n</i> -Bu ₄ N) ₂ W ₂ O ₁₁	TL 27 2617 (1986)
H ₂ O ₂ , cat H ₃ [PW ₁₂ O ₄₀], cat [C ₅ H ₅ N(CH ₂) ₁₅ CH ₃]Cl	JOC 53 3587 (1988) JACS 117 681 (1995)
H ₂ O ₂ , cat tetrakis(diperoxotungsto)phosphates	JOC 53 1553 (1988)
H ₂ O ₂ , cat chloromanganese(tetra-2,6-dichloro- phenylporphyrin), imidazole	CC 888 (1985)
H ₂ O ₂ , cat chiral Mn(dihydrosalen), imidazole (enantioselective)	TL 34 4785 (1993)
H ₂ O ₂ , cat chiral Mn(III)-salen, cat imidazole (enantioselective)	TL 35 941 (1994)
H ₂ O ₂ , cat chiral Mn(III)-salen, cat <i>N</i> -methyl- imidazole (enantioselective)	SL 255 (1994)
H ₂ O ₂ , Fe(acac) ₃	TL 948 (1978)
H ₂ O ₂ , cat Fe porphyrin	JACS 115 2775 (1993)
H ₂ O ₂ , Cl ₂ CHCOCHCl ₂ , Na ₂ HPO ₄	TL 22 2089 (1981)
H ₂ O ₂ , CF ₃ COCF ₃	JACS 101 2484 (1979)
H ₂ O ₂ , HCONH ₂ , NaH ₂ PO ₄	TL 36 4015 (1995)
H ₂ O ₂ , H ₂ NCONH ₂ , Na ₂ HPO ₄ , Ac ₂ O or (CF ₃ CO) ₂ O	SL 533 (1990)
H ₂ O ₂ , CH ₃ CN, NaOH	JOC 26 659 (1961)
H ₂ O ₂ , CH ₃ CN, KHCO ₃	Org Syn 60 63 (1981) Org Syn Coll Vol 7 126 (1990)
H ₂ O ₂ , Cl ₃ CCN, NaOH	JOC 26 659 (1961)
H ₂ O ₂ , Cl ₃ CCN, K ₂ HPO ₄	JOC 48 888 (1983)

- H_2O_2 , PhCN, NaOH JOC 26 659 (1961)
 H_2O_2 , PhCN, NaHCO_3 Austral J Chem 39 411 (1986)
 H_2O_2 , PhCN, KHCO_3 Tetr 18 763 (1962)
 JOC 32 1363 (1967); 36 3832 (1971); 50 2179 (1985)
 JCS C 731 (1970)
 JACS 95 6853 (1973); 106 3539 (1984)
 TL 35 6051 (1994)
 H_2O_2 , PhCN, K_2CO_3 JOC 32 1363 (1967)
 H_2O_2 , $(\text{EtO})_2\text{POCN}$, 2-hydroxypyridine Chem Pharm Bull 29 1774 (1981)
 H_2O_2 , $\left[\begin{array}{c} \text{N} \\ | \\ \text{Me} \end{array} \right] \text{Cl} \text{PO}_2\text{Cl}_2^-$, Na_2CO_3 JOC 56 469 (1991)
 H_2O_2 , $\text{Ph}_2\text{P}(\text{O})\text{O}(\text{O})\text{PPh}_2$ TL 35 8123 (1994)
 90% H_2O_2 , $\text{CH}_3\text{C}(\text{OEt})_3$ TL 1001 (1979)
 H_2O_2 , $\left(\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \right)_2\text{CO}$ CC 711 (1974)
 JOC 43 180 (1978); 44 1485 (1979)
 H_2O_2 , EtO_2CCl , Na_2HPO_4 or $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ JOC 44 2569 (1979)
 H_2O_2 , ArNCO (Ar = Ph, *p*- ClC_6H_4) TL 2029 (1970)
 H_2O_2 , PhCONCO CC 711 (1974)
 JOC 43 180 (1978); 44 1485 (1979)
 H_2O_2 , cat chloroperoxidase (enantioselective) JACS 115 4415 (1993); 117 6412 (1995)
t-BuO₂H, molecular sieves (allylic alcohols) TL 33 3205 (1992)
t-BuO₂H, Al(O-*t*-Bu)₃ (allylic alcohols) TL 27 3387 (1986)
t-BuO₂H, SiO₂ TL 36 3825 (1995)
t-BuO₂H, *n*-Bu₂SnO (allylic alcohols) TL 27 3387 (1986)
t-BuO₂H, Ti(O-*i*-Pr)₄ (allylic alcohols) TL 27 3387 (1986); 33 3461 (1992)
 JACS 110 2978 (1988); 115 7226 (1993)
t-BuO₂H, Ti(O-*i*-Pr)₄, dialkyl tartrate (allylic alcohols, Sharpless, enantioselective) JACS 102 5974 (1980); 103 464, 6237 (1981); 107 1691, 7515, 7967 (1985); 108 2776 (1986); 109 1525, 2205, 4718 (1987); 110 2978, 4672, 5195 (1988); 113 106, 113 (1991) (both mechanism)
 Tetr 37 3873 (1981)
 Pure Appl Chem 55 589, 1823 (mechanism) (1983)
 Org Syn 63 66 (1984)
 JOC 49 1707 (1984); 50 3752 (1985); 51 934, 1077, 4726, 4728 (1986); 52 685, 940, 1106 (1987); 55 1693 (1990); 56 1758 (1991); 57 4441 (1992)
 "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1985), Vol 5, Chpts 7, 8 (reviews)
 CC 1759 (1985); 1237, 1732 (1986)

- TL 27 3535, 4913 (1986); 28 375, 1139, 2033, 3075, 4019, 4985, 6351 (1987); 30 4303, 6637 (1989); 34 1327 (1993); 35 2873 (1994)
 Syn 89 (1986) (review)
 Angew Int 25 87 (1986)
 CL 1523 (1987)
 Org Syn Coll Vol 7 461 (1990)
- t*-BuO₂H, Ti(O-*i*-Pr)₄, diethyl tartrate, cat CaH₂, cat silica gel (enantioselective) TL 26 6221 (1985)
 JACS 111 1057 (1989)
- t*-BuO₂H, Ti(O-*i*-Pr)₄, diisopropyl tartrate, molecular sieves (enantioselective) TL 33 5365 (1992)
- t*-BuO₂H, Ti(O-*i*-Pr)₄, various chiral diols, molecular sieves (enantioselective) JOC 54 2826 (1989)
- t*-BuO₂H, cat Ti(O-*i*-Pr)₄, cat dialkyl tartrate, molecular sieves (allylic alcohols, enantioselective) TL 27 5791 (1986); 28 131, 5129, 5205 (1987); 31 5023, 6983 (1990); 32 3527, 5137 (1991); 33 7043 (1992); 34 1629 (1993)
 JOC 51 1922 (1986); 52 940, 2596 (1987); 54 2817 (1989); 56 741 (1991); 57 6025 (1992)
 JACS 109 5765, 8120 (1987); 113 2786 (1991)
 SL 279, 548, 811 (1991)
- t*-BuO₂H, Ti(O-*t*-Bu)₄, several bis(tartrate) esters (enantioselective) JOC 54 4016 (1989)
- PhCMe₂O₂H, cat Ti(O-*i*-Pr)₄, cat diisopropyl tartrate, molecular sieves (allylic alcohols, enantioselective) JOC 51 3710, 5413 (1986); 52 4973 (1987)
 JACS 109 5765, 8120 (1987)
 TL 29 2139 (1988); 31 5023 (1990)
- RO₂H, cat Ti(O-*i*-Pr)₄, cat peptide or amino acid, molecular sieves (enantioselective) JOC 57 6329 (1992)
- Ph₃CO₂H, Ti(O-*i*-Pr)₄, diethyl tartrate, molecular sieves (enantioselective) TL 29 3171 (1988)
- t*-BuO₂H, Zr(O-*i*-Pr)₄, dicyclohexyl tartramide (homoallylic alcohols, enantioselective) CL 85 (1987)
- t*-BuO₂H, cat V₂O₅ TL 32 3167 (1991)
- t*-BuO₂H, cat VO(acac)₂ (allylic and homoallylic alcohols) JACS 95 6136 (1973); 96 5254 (1974); 103 7690 (1981); 107 256 (1985); 110 3585, 6192 (1988); 113 3096 (1991)
 CC 421 (1976)
 TL 2741 (1978); 4733 (1979); 27 3353, 3387, 6035, 6071 (1986); 28 1439, 2099, 6191 (1987); 29 2449 (1988); 32 6943 (1991); 33 2455, 3461 (1992); 34 611, 2295 (1993)
 JOC 51 4728 (1986); 52 34, 4495, 4511, 4898 (1987); 57 6025 (1992); 58 7929 (1993)
- PhCMe₂O₂H, cat VO(acac)₂, 2,6-lutidine (allylic alcohol) JACS 109 6187 (1987)

- t*-BuO₂H, cat VO₂O₄ or MoO₂(acac)₂, (+)-3-trifluoroacetylcamphor
Z Chem 18 218 (1978)
- t*-BuO₂H, cat VO(O-*n*-Pr)₃
TL 31 31 (1990)
- t*-BuO₂H, cat Mo(CO)₆ (primarily allylic and homoallylic alcohols)
JACS 95 6136 (1973); 96 5254 (1974); 110 8129 (1988) (no alcohol present); 113 3096, 4037 (1991); 114 9419 (1992)
TL 2741 (1978); 4733 (1979); 31 4301 (1990); 32 1707 (1991)
JOC 51 2505 (1986)
- t*-BuO₂H, cat MoO₂(acac)₂, cat amine
TL 29 2843 (1988)
- t*-BuO₂H, cat 
TL 29 971 (1988)
- t*-BuO₂H, polystyrene-Mo catalyst
TL 29 971 (1988)
- t*-BuO₂H, cat Fe porphyrin
JACS 115 2775 (1993)
- t*-BuO₂H, cat Ln(O-*i*-Pr)₃ (Ln = La, Ce, Sm, Yb), molecular sieves
TL 32 2355 (1991)
- Ph₃SiO₂H
TL 4337 (1979)
- 
JOC 47 1141 (1982)
-  (enantioselective)
JOC 56 809 (1991)
- RSO₂N-O-CHAr (enantioselective)
JACS 105 3123 (1983)
TL 27 5079 (1986)
- NMO, cat RuCl₃
Ind J Chem A 27 873 (1988)
- 
TL 29 3941 (1988)
- heterocyclic N-oxide, cat Ru porphyrin
TL 30 6545 (1989); 32 7435 (1991); 33 2521 (1992)
- air, cat Ni-montmorillonite, Me₂CHCHO
TL 34 1123, 1127 (1993)
- O₂, RCHO
TL 33 6827 (1992)
- O₂, CH₃CHO
Syn 711 (1977)
- O₂, PhCOCHOHPh, hν
JACS 103 2049 (1981)

- O_2 , Me_2CHCHO , cat NPV_6Mo_6 JOC 58 6421 (1993)
- O_2 , cat Mn porphyrin JACS 106 6871 (1984)
- O_2 , cat $[Fe_3O(O_2CR)_6L_3]^+$ JACS 104 6450 (1982)
- O_2 , cat Fe porphyrin, Me_2CHCHO TL 34 6033 (1993)
- O_2 , cat $Fe[2-(\text{acetoacetoxy})\text{ethyl methacrylate}]_3$,
 Me_2CHCHO TL 35 3633, 4193 (1994)
- O_2 ,  cat Co(II) TL 34 4657 (1993)
- O_2 , Me_2CHCHO , cat Co(II) Schiff's base JOC 59 850 (1994)
 TL 36 159 (1995)
- O_2 , Me_2CHCHO , cat  TL 32 6891 (1991)
- O_2 , Me_2CHCHO ,
 cat  OAc (R = H, Ph) SL 641 (1992)
- $NaBO_3 \cdot 4H_2O$, Ac_2O TL 29 2967 (1988)
- $KMnO_4$, $CuSO_4$ JOC 57 1928 (1992)
- $MO_5 \cdot HMPT$ (M = Mo, W) JOC 51 2374 (1986)
 TL 28 6191 (1987) (homoallylic *i*-Pr₃Si ethers)
- SeO_2 or $(PhSeO)_2O$, cat $[(p\text{-}BrC_6H_4)_3N^+]$ JACS 113 3613 (1991); 115 7653 (1993)
 $SbCl_6^-$ (styrenes, 1,3-dienes)
- $PhIO$, cat chiral Cr(salen), Ph_3PO (enantioselective) TL 36 7739 (1995)
- $ArIO$, cat chiral Mn salen complex (enantioselective) JACS 112 2801 (1990)
 TL 31 7345 (1990); 32 1055 (1991); 33
 1001 (1992)
 SL 691 (1991); 407 (1992); 261, 641 (1993); 356,
 479 (1994); 197, 407 (enyne) (1995)
- $PhIO$, cat chiral Mn salen complex, pyridine
N-oxide (enantioselective) SL 265 (1991); 300 (1993)
- $PhIO$, cat chiral Mn salen complex, 2-methyl-
 imidazole (enantioselective) SL 265 (1991); 300 (1993)
- $PhIO$, cat Mn salen-polymer TL 34 2371 (1993)

- PhIO, cat Mn porphyrins (enantioselective) TL 32 4901 (1991)
JACS 114 1313 (1992); 115 7653 (1993)
- PhIO, cat Mn porphyrin, dicyclohexylimidazole (enantioselective) JACS 115 3834 (1993); 117 692 (1995)
- PhIO, cat Mn or Fe porphyrin on a solid support TL 33 2737 (1992)
- PhIO or C₆F₅IO, cat Mn or Fe binaphthalene-linked porphyrin (enantioselective) TL 33 6323 (1992)
- PhIO, cat Fe porphyrin (enantioselective) TL 32 4901 (1991)
- PhIO, Co catalyst JOC 52 4545 (1987)
- chiral Cr-salen, Ph₃PO (enantioselective) TL 36 7739 (1995)
- NBS, H₂O/base TL 121 (1962); 30 3935 (1989); 35 6997 (1994)
JACS 85 3295 (1963); 90 5618 (1969)
JOC 38 1385 (1973); 51 5447 (1986); 52 4505 (1987); 59 2204 (1994); 60 4905, 5726 (1995)
JCS Perkin I 2909 (1982)
Org Syn Coll Vol 6 560 (1988)
- NIS, H₂O/DBU JOC 51 2505 (1986)
- CH₃CONHBr, H₂O/base JOC 51 3407 (1986); 52 2860 (1987); 58 3761 (1993); 59 1389 (1994)
- 1,3-dibromo-5,5-dimethylhydantoin, H₂O/NaOH TL 27 4403 (1986)
- F₂, H₂O, CH₃CN Angew Int 25 554 (1986)
JOC 55 5155 (1990); 56 3187 (1991); 58 972 (1993)
- I₂, H₂O, HI/NaOH JCS C 928 (1970)
- I₂, Ag₂O, H₂O TL 207 (1976)
JOC 51 3023 (1986)
- I₂, Ag₂O, H₂O/DBU JOC 59 4316 (1994)
- LiOCl, cat Mn porphyrin chloride, R₄NCl, base JACS 112 7980 (1990)
- NaOCl, cat chiral Mn(III)-salen (enantioselective) TL 32 6533 (1991) (1,3-diene and enyne); 33 1001 (1992); 35 8927 (1994)
JACS 113 6703, 7063 (1991)
JOC 56 2296 (1991); 57 4320 (1992); 58 6939 (1993) (1,3-diene); 59 1939 (1994)
SL 197, 407 (enyne) (1995)
- NaOCl, cat chiral Mn(III)-salen, cat 4-phenylpyridine *N*-oxide (enantioselective) TL 35 669 (1994) (1,3-dienes); 36 5123 (1995)
JOC 59 4378 (1994)
SL 827 (1995) (1,3-dienes)
- NaOCl, cat chiral Mn(III)-salen, *N*-benzylquininium chloride (enantioselective, *cis*-alkene to *trans*-epoxide) JACS 116 6937 (1994)
- NaOCl, cat Mn porphyrin, Aliquat, *n*-hexylimidazole JOC 53 2863 (1988)

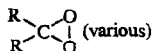
- NaOCl, cat chiral Mn porphyrin, cat R_4NCl ,
cat 4-*t*-Bu-pyridine (enantioselective) JOC 56 5253 (1991)
- NaOCl, cat Mn porphyrin acetate, R_4NCl , py JACS 106 6668 (1984)
- bleach, cat chiral Mn(III)-salen (enantioselective) TL 32 5055 (1991)
- $NaIO_4$ or (*n*-Bu₄N)IO₄, cat chiral Mn(III)-salen
(enantioselective) TL 36 319 (1995)
- (*n*-Bu₄N)IO₄, cat Mn tetraphenylporphyrin,
cat imidazole TL 35 945 (1994)
- $NaIO_4$, cat $RuCl_3 \cdot 3H_2O$, bidentate ligand TL 36 8775 (1995)
- Oxone® ($K_2SO_4 \cdot 2KHSO_5 \cdot KHSO_4$) JOC 59 374 (1994)
TL 36 833 (1995)
- $KHSO_5$, acetone, 18-crown-6 JOC 45 4758 (1980)
- $KHSO_5$, CH_3COCH_3 , $Na_2(EDTA)$, 18-crown-6,
 CH_2Cl_2 , H_2O JOC 47 2670 (1982)
- $KHSO_5$, $Na_2(EDTA)$, (*n*-Bu₄N)HSO₄, KOH, buffer,
3-trifluoroacetylcamphor or $PhC(CF_3)(OMe)-$
 $COCH_3$ (enantioselective) TL 36 5831 (1995)
- $KHSO_5$, various ketones TL 35 1577 (1994)
- $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, $NaHCO_3$, H_2O JOC 56 7022 (1991)
- $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$,
cat $\left[O = \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \end{array} \begin{array}{c} \text{CH}_3 \\ | \\ \text{N} \\ | \\ n\text{-C}_{12}\text{H}_{25} \end{array} \right] \text{OTf, buffer}$ JOC 60 1391 (1995)
- $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, acetone, 18-crown-6,
 CH_2Cl_2 , H_2O JOC 50 2847 (1985)
- $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array} \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \end{array} \begin{array}{c} \text{O} \\ | \\ \text{O} \end{array}$ JOC 53 1338, 3437 (1988); 54 4249 (1989); 55 4211,
5929 (1990); 56 1153 (allenes), 3677 (1991); 57
2182, 5979, 6379 (1992); 58 3761, 7204 (1993);
59 1892, 1895 (1994); 60 3692 (1995)
JACS 110 7929 (1988); 111 6661 (1989); 114 4518
(1992); 115 3146, 7152, 8473, 8603 (1993); 117
5693, 5701, 5712, 5720 (1995)
TL 30 123, 4223, 6497 (1989); 31 2047, 5235, 6517
(1990); 32 533, 1041, 1295, 4035, 6697 (1991); 33
4053, 6097 (1992); 34 8427 (1993); 35 6977, 9131
(1994); 36 2437, 3673, 4991, 6475, 7111 (1995)
Chem Rev 89 1187 (1989) (review)
Acct Chem Res 22 205 (1989) (review)
- $\begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{C} \\ \diagup \\ \text{CH}_3 \end{array} \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \end{array} \begin{array}{c} \text{O} \\ | \\ \text{O} \end{array}$, cat chiral Mn(III)-salen
(enantioselective) TL 36 3669 (1995)



JOC 53 3890 (1988); 60 3692, 3887 (1995)
TL 30 257 (1989)



JACS 114 1346 (1992)



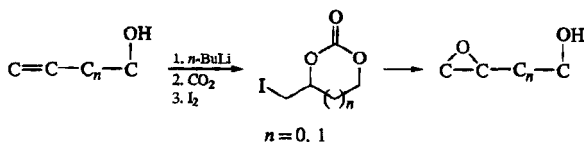
TL 32 533 (1991)

H₂O, NaBr, electrolysis

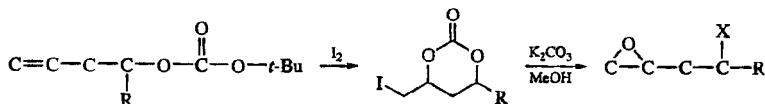
TL 4661 (1979)
JOC 46 3312 (1981); 50 3160 (1985)

H₂O, [polymer-NR₃]⁺Br⁻, electrolysis

JOC 47 3575 (1982)

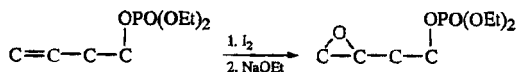


CC 465 (1981)
JOC 47 4626 (1982); 52 3560 (1987)



X = OH or OCO₂Me

JOC 47 4013 (1982)



JACS 99 4829 (1977)



Review: Topics Stereochem 7 93 (1973)

X

Reagent(s)

COR

H₂O₂, NaHCO₃

JACS 103 3460 (1981)
JOC 52 4647 (1987)

H₂O₂, K₂CO₃

JOC 52 3560 (1987)

H₂O₂, LiOH

TL 28 2099 (1987)

H₂O₂, NaOH

Ber 54 2327 (1921)

Helv 25 836 (1942)





JACS 79 1488 (1957); 105 2435 (1983); 109
4690 (1987); 113 1355 (1991)

- H_2O_2 , NaOH, H_2NCONH_2 Org Syn Coll Vol 4 552 (1963); 6 679 (1988)
 H_2O_2 , NaOH, various poly- Tetr 19 1091 (1963)
 (amino acids) (enantioselective) JOC 50 2981, 3957 (1985); 51 3098 (1986); 53
 1515 (1988); 54 4072 (1989); 55 227 (1990);
 H_2O_2 , NaOH, poly-L or D-alanine 56 2076, 5572 (1991); 57 1151, 2757 (1992)
 (enantioselective) SL 533 (1990)
 H_2O_2 , NaOH, poly-L-leucine JOC 55 6047 (1990)
 (enantioselective) TL 28 4857 (1987)
 H_2O_2 , cat $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, H_2O TL 31 6501 (1990)
 H_2O_2 or *t*-BuO₂H, NaOH, chiral JOC 58 6247 (1993)
 R_4NCl (enantioselective) TL 36 4125 (1995)
 Chimia 30 445 (1976)
 CC 427 (1978)
 JOC 45 2498 (1980)
 H_2O_2 or *t*-BuO₂H, *n*-Bu₄F CL 285 (1987)
t-BuO₂H, KF-Al₂O₃ TL 35 9481 (1994)
t-BuO₂H, cat bovine serum albumin, TL 28 1577 (1987)
 buffer (enantioselective)
t-BuO₂H, NaOH JACS 106 4558 (1984)
 JOC 57 7118 (1992)
t-BuO₂H, Triton-B JACS 80 5845 (1958); 99 5773 (1977); 115
 3966 (1993)
 TL 36 6611 (1995)
t-BuO₂H, DBU JACS 107 1777 (1987)
t-BuO₂H, RLi CC 1378 (1986)
 JACS 116 11287 (1994)
t-BuO₂H, KH JACS 101 2493 (1979); 106 4038 (1984)
 TL 27 1343, 6189 (1986)
 JOC 51 3393 (1986)
t-BuO₂H, KO-*t*-Bu TL 32 4477 (1991)
 magnesium monoperoxyphthalate TL 36 837 (1995)
 NaBO₃, NaOH, (*n*-Hex₄N)HSO₄ TL 36 663 (1995)
 F₂, H₂O, CH₃CN Angew Int 25 554 (1986)
 NaOCl, py JOC 28 250 (1963)
 NaOCl, (*n*-Bu₄N)HSO₄ Gazz Chim Ital 110 267 (1980)
 $\text{CH}_3-\text{C}(\text{O})-\text{O}-\text{CH}_3$ SL 323 (1996)
 TL 31 331 (1990); 34 5055 (1993)
 Ber 124 227 (1991)
 JOC 56 7292 (1991); 57 2182 (1992); 58 7615
 (1993); 59 900, 4304 (1994)
 $\text{CH}_3-\text{C}(\text{O})-\text{O}-\text{CF}_3$ JOC 60 3887 (1995)
 $\text{Me}-\text{C}(\text{O})-\text{O}-\text{Et}$ Ber 124 227 (1991)

CO₂H

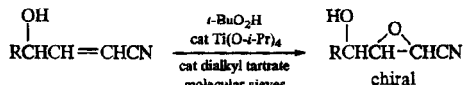
H_2O_2 , cat $\text{Na}_2\text{WO}_4 \cdot \text{H}_2\text{O}$
 H_2O_2 , Na_2WO_4 , py

JOC 24 54 (1959); 50 1979 (1985)
 TL 33 5265 (1992)

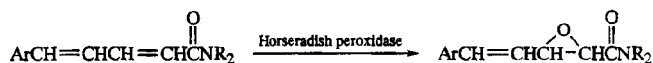
X	<u>Reagent(s)</u>	
	magnesium monoperoxyphthalate	TL 36 837 (1995)
	Oxone® (K ₂ SO ₄ ·2KHSO ₅ ·KHSO ₄)	TL 36 833 (1995)
	KHSO ₅ , CH ₃ COCH ₃ , NaHCO ₃	JOC 51 1925 (1986)
	KHSO ₅ , CH ₃ COCH ₃ , (18-crown-6)	JOC 45 4758 (1980)
		TL 31 331 (1990)
		JOC 58 7615 (1993)
		JOC 60 3887 (1995)
	CO ₂ R	
	<i>t</i> -BuO ₂ Li	CC 1378 (1986)
	<i>t</i> -BuO ₂ Li, (Me ₄ N)ClO ₄	TL 34 2469 (1993)
	<i>t</i> -BuO ₂ H, KO- <i>t</i> -Bu	TL 34 1039 (1993)
	<i>t</i> -BuO ₂ H, Triton B	TL 32 4477 (1991)
	<i>t</i> -BuO ₂ H, Triton B	TL 34 1039 (1993)
		TL 31 331 (1990)
		JOC 58 7615 (1993)
		JOC 60 3887 (1995)
	F ₂ , H ₂ O, CH ₃ CN	Angew Int 25 554 (1986)
	NaOCl, DMF	Heterocycles 24 1137 (1986)
		JOC 58 6779 (1993)
	AgOAc, bipy, electrolysis	TL 35 3695 (1994)
	SO ₂ R	
	H ₂ O ₂ , NaOH	JOC 53 2398 (1988); 58 5221 (1993)
	NaOOH	TL 34 5007 (1993)
	<i>t</i> -BuO ₂ Li	TL 32 5393 (1991); 33 6197 (1992); 34 5007 (1993)
		JOC 59 6419 (1994)



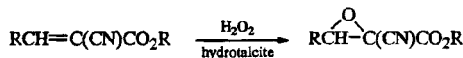
X	<u>Reagents</u>	
R	H ₂ O ₂ , NaOH	TL 31 4509 (1990); 32 2687 (1991)
	PhCMe ₂ O ₂ H, NaOH, R ₄ NBr	TL 31 4509 (1990)
	<i>t</i> -BuO ₂ H, NaOH	TL 31 4509 (1990); 32 2687 (1991)
	<i>t</i> -BuO ₂ H, Ti(O- <i>i</i> -Pr) ₄	TL 31 4509 (1990); 32 2687 (1991)
	<i>t</i> -BuO ₂ H, VO(acac) ₂	TL 32 2687 (1991)
OR	<i>t</i> -BuO ₂ H, Ti(O- <i>i</i> -Pr) ₄	TL 32 2687 (1991)



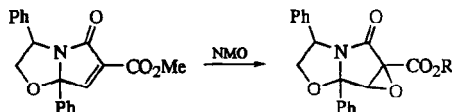
TL 32 2045 (1991)



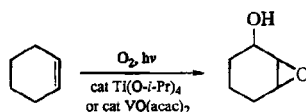
TL 35 279 (1994)



TL 36 4125 (1995)

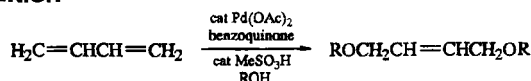


TL 36 1613 (1995)

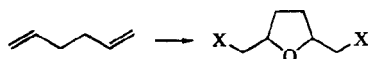


JACS 111 203 (1989)

6. Diene Addition



JOC 53 5695 (1988)



X

Reagents

SePh

PhSeCl, H₂O

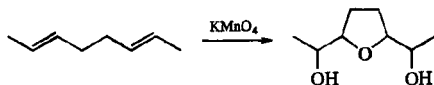
JOC 44 1742 (1979)

Tetr 41 5301 (1985)

HgX

HgX₂, H₂O

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 2 (review)

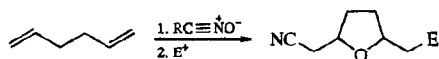


Tetr 21 2353 (1965)

JACS 101 4396 (1979); 112 5624 (1990)

TL 21 3531 (1980); 28 731 (1987); 34 5847 (1993)

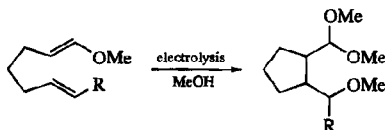
JOC 48 5404 (1983)



R = Ph₃C, Me₃C, Me₃Si, R'CH(OSiMe₃); E⁺ = Br₂, I₂, PhSeBr

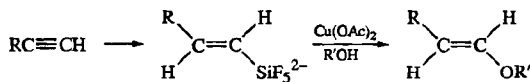
JACS 109 7577 (1987); 114 10061 (1992)

JOC 55 283 (1990)

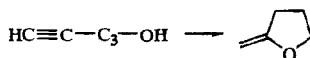


JACS 112 6123 (1990); 113 7372 (1991); 114 1033 (1992) (R = OR)

7. Alkyne Addition



Organomet 1 369 (1982)



cat AgO

TL 28 6447 (1987)

cat AgOAc

TL 28 6447 (1987)

cat Ag₂CO₃

TL 28 6447 (1987)

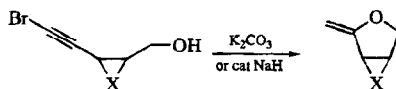
HgCl₂, Et₃N

JACS 104 5842 (1982)

Hg(O₂CCF₃)₂/NaBH₄, NaOMe

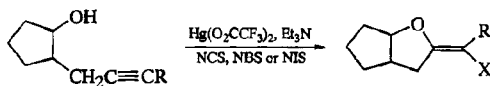
TL 24 1187 (1983)

Angew Int 23 847 (1984)



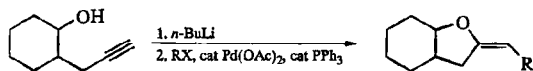
X = O, CH₂

TL 33 4905 (1992)



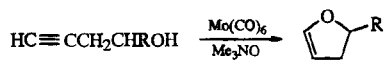
X = Cl, Br, I

JACS 104 5842 (1982)



R = Me, PhCH₂, aryl

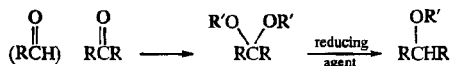
JOC 57 2213 (1992)



JOC 58 6952 (1993)

4. ACETAL, CARBONYL AND ORTHO ESTER CONVERSIONS

1. Acetals



Reviews:

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 8, Part 1.9, p 211
SL 97 (1992) (bicyclic acetals)

Reducing agent

H ₂ , cat Rh-alumina, H ⁺	JOC 26 1026 (1961)
H ₂ , cat Ni	JACS 54 1651 (1932)
H ₂ , cat PtO ₂ , H ⁺	JCS 5598 (1963)
H ₂ , CO, cat Co ₂ (CO) ₈ (R = aryl)	Can J Chem 54 685 (1976)
BH ₃	Curr Sci 404 (1963) Can J Chem 52 888 (1974) JOC 53 5179 (1988)
BH ₃ ·SMe ₂ , Me ₃ SiOTf	TL 32 1095 (1991) JOC 58 6756 (1993)
ClBH ₂ ·OEt ₂	CL 9 (1984)
ClBH ₂ ·SMe ₂	JOC 53 5179 (1988) TL 32 3719 (1991)
Cl ₂ BH	JCS Perkin I 1807 (1981)
CB	JOC 42 512 (1977)
NaBH ₄ , CF ₃ CO ₂ H (R = aryl)	Org Prep Proc Int 17 11 (1985)

NaBH ₃ CN, HCl	TL 1357 (1978) SL 925 (1995)
NaBH ₃ CN, cat <i>n</i> -Bu ₃ SnCl	SL 95 (1995)
Zn(BH ₄) ₂ , Me ₃ SiCl	JOC 52 2594 (1987)
Et ₂ AlF, 2 C ₆ F ₅ OH	JACS 115 10695 (1993)
Al(OC ₆ F ₅) ₃	JACS 115 10695 (1993) SL 127 (1993)
<i>i</i> -Bu ₃ Al	TL 28 4181 (1987) (chiral)
<i>i</i> -Bu ₂ AlH	Izv Akad Nauk SSSR, Ser Khim 2255 (1959) [CA 54 10837h (1960)] Ber 113 3697 (1980) TL 24 4581 (1983) (chiral); 27 983 (1986) (chiral); 29 4085 (1988); 34 5303 (1993) CL 1593 (1983) JOMC 285 83 (1985) (chiral) Syn 811 (1986) JOC 54 5153 (1989); 57 4580, 7285 (1992); 58 4555 (1993); 59 1358 (1994) Tetr 46 4595 (1990)
Cl ₂ AlH	CC 334 (1987) (chiral) Tetr 46 4595 (1990)
Br ₂ AlH	TL 24 4581 (1983); 27 983, 987 (1986) (all chiral) JOMC 285 83 (1985) (chiral) CC 334 (1987) (chiral) Tetr 46 4595 (1990)
LiAlH ₄ /BF ₃ ·OEt ₂	JOC 27 67 (1962)
LiAlH ₄ , AlCl ₃	JOC 23 1088 (1958); 26 4553 (1961); 27 67 (1962) JACS 81 6087 (1959); 84 2371 (1962); 107 3891 (1985) Org Syn Coll Vol 5 303 (1973) TL 34 5373 (1993)
LiAlH ₄ , TiCl ₄ (R = alkyl)	BCSJ 51 2059 (1978)
Ph ₂ SiH ₂ , TiCl ₄	Tetr 46 4595 (1990) TL 34 5303 (1993)
Et ₃ SiH, Nalfion-H	JOC 51 2826 (1986)
Et ₃ SiH, cat TfOH, cat bis(trimethylsilyl)- acetamide or bis(trimethylsilyl)urea	SL 433 (1993)
Et ₃ SiH, cat FSO ₃ H, cat bis(trimethylsilyl)- acetamide or bis(trimethylsilyl)urea	SL 583 (1993)
Et ₃ SiH, CF ₃ CO ₂ H	JOC USSR 8 902 (1972) TL 36 669 (1995)
Et ₃ SiH, CF ₃ CO ₂ H, BF ₃ ·OEt ₂	JACS 104 3539 (1982); 109 8117 (1987)

Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$ Et_3SiH , cat $n\text{-Bu}_2\text{Sn}(\text{OTf})_2$ Et_3SiH , SnCl_4 Et_3SiH , TiCl_4 R_3SiH ($\text{R} = \text{Me}, \text{Et}$), cat Me_3SiOTf R_3SiH ($\text{R} = \text{Me}, \text{Et}, n\text{-Pr}$), cat ZnCl_2

Carbohydr Res 128 C9 (1984)

JACS 112 901 (1990) (ketals only)

Tetr 46 4595 (1990)

TL 34 5303 (1993)

JOC 60 5048 (1995)

TL 27 987 (1986) (chiral); 34 575 (1993)

JACS 109 527 (1987) (chiral)

JOC 54 5153 (1989); 57 5036 (1992)

Tetr 46 4595 (1990)

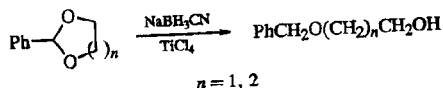
TL 4679 (1979)

JOC 52 892 (1987); 60 4264 (1995)

Compt Rend 254 1814 (1962)

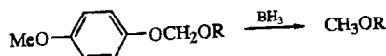


TL 33 5045 (1992)

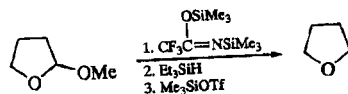
 $n = 1, 2$

Syn 373 (1988)

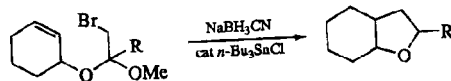
JACS 117 8017 (1995)



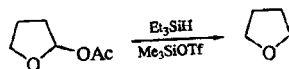
TL 34 1991 (1993)



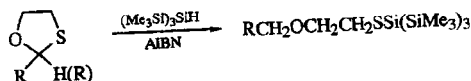
JOC 52 892 (1987)



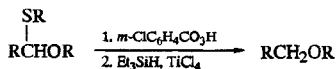
TL 36 1127 (1995)



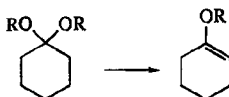
TL 36 3627 (1995)



TL 32 2853 (1991)



JACS 111 4136 (1989)



cat TsOH

JCS C 1477 (1971)

Syn 38 (1974)

Acta Chem Scand 28B 357 (1974)

cat 2,4,6-Me₃C₆H₂SO₃H

Tetr 21 1673 (1965)

PhCO₂H, succinic anhydride, py

JOC 38 2910 (1973)

cat H₃BO₃

JACS 60 1159 (1938)

cat (NH₄)H₂PO₄

JOC 28 3362 (1963)

cat HCl

Ber 102 1892 (1969)

MgBr₂, Et₃N

Helv 62 1451 (1979)

AlCl₃, Et₃N

Helv 62 1451 (1979)

i-Bu₃Al

TL 27 1363 (1986)

JOC 55 5814 (1990); 57 5438 (1992)

t-BuCH(Cy)N(*t*-Bu)Al(*i*-Bu)₂

TL 27 1363 (1986)

Me₃SiOTf, *i*-Pr₂NEt

JOC 53 5574 (1988); 58 1449 (1993)

Me₃SiCl, cat PhCO₂H, py

JOC 59 1889 (1994)

Me₃SiCl, NaI, Et₃N

JOC 59 1889 (1994)

Me₃SiI, (Me₃Si)₂NH

TL 23 323 (1982)

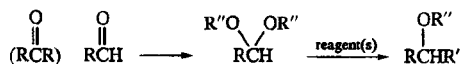
Me₃SiMn(CO)₅

TL 23 631 (1982)

Organomet 1 1467 (1982)

TiCl₄/DBU

TL 27 3053 (1986)

Reagent(s)R'Li, TiCl₄

TL 25 3947 (1984) (chiral); 35 1913 (1994) (chiral)

R'MgX

JACS 73 4893 (1951)

Rec Trav Chim 81 238 (1962)

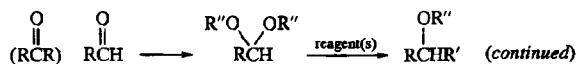
Organomet 1 1670 (1982)

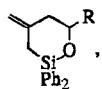
JOC 59 8192 (1994)

R'MgX, BF₃·OEt₂

TL 35 1913 (1994) (chiral)

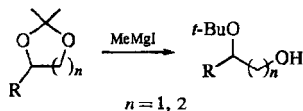
$R'MgX$, $TiCl_4$	BCSJ 54 776 (1981) TL 25 3947 (1984) (chiral); 35 1913 (1994) (chiral) JOC 54 3282 (1989)
$H_2C=CHCH_2M$ ($M = B \begin{smallmatrix} \diagup \diagdown \end{smallmatrix}$, SnR_3), Lewis acid?	JACS 108 7116 (1986) (chiral)
$H_2C=CHCH_2B \begin{smallmatrix} \diagup \diagdown \end{smallmatrix}$, $TiCl_4$	CC 1218 (1987) (chiral)
$Me_3SiOTf / [(H_2C=CHCH_2)_3B-n-Bu]Li$	TL 30 2013 (1989)
R'_3Al	JOC 54 5539 (1989) JACS 115 10695 (1993)
$Me_3Al / Me_2AlC \equiv CR$	JOC 54 5539 (1989)
Me_3Al / Me_3SiOTf	JOC 60 4264 (1995)
R'_3Al , $TiCl_4$	TL 30 2967 (1989)
Et_2AlCl	TL 34 967 (1993)
R'_2AlOAr	JACS 115 10695 (1993)
$H_2C=CHCH_2Br$, Al , cat $AlBr_3$, cat $PbBr_2$	TL 29 1721 (1988)
$RCH=CRCH_2Al_{2/3}Br$	JOMC 170 1 (1979)
$H_2C=CHCH_2SiCl_3$, cat $n-Bu_2Sn(OTf)_2$	JACS 112 901 (1990) (ketals only)
$RCH=CRCHRSiMe_3$, review (diastereoselective)	Chem Rev 95 1293 (1995)
many Lewis acids	JACS 111 3475 (1989)
cat $TfOH$, cat bis(trimethylsilyl)acetamide or bis(trimethylsilyl)urea	SL 433 (1993)
cat FSO_3H , cat bis(trimethylsilyl)urea	SL 583 (1993)
cat Ph_2BOTf	CL 977 (1985)
$BF_3 \cdot OEt_2$	CL 941 (1976) TL 2589 (1978); 21 951 (1980) JOC 48 335 (1983); 54 98 (1989); 57 2888 (1992) JACS 111 3475 (1989) SL 43 (1994)
$AlCl_3$	CL 575 (1978)
Me_3SiI	TL 22 745 (1981)
Me_3SiOTf	TL 21 71, 2527 (1980); 23 723 (1982); 31 2063 (1990); 33 2847, 5981 (1992); 36 1003, 1263 (1995) JOC 52 892 (1987); 56 5755 (1991); 58 1003 (1993) JACS 111 3475 (1989); 117 10587 (1995)
$SnCl_4$	JCS Perkin I 251 (1981) (intramolecular) JACS 104 7371 (1982) (chiral); 110 8698 (1988); 111 3475 (1989); 115 40 (1993)

**Reagent(s)**

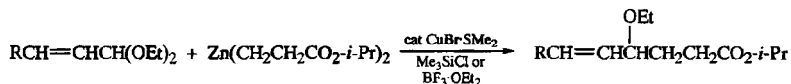
$\text{SnCl}_4, \text{TiCl}_4$	JACS 111 8277 (1989) (intramolecular)
TiCl_4	CL 941 (1976); 575 (1978) TL 2589 (1978); 429 (1979); 21 951, 2049 (1980); 23 725 (1982); 28 6343 (1987); 34 575 (1993); 36 357 (1995) JACS 105 2088 (1983) (chiral); 108 7116 (1986) (chiral); 111 3475 (1989) CC 1218 (1987) (chiral) JOC 54 3282 (1989); 56 6458, 6485 (1991); 60 7830 (1995) SL 702 (1991); 114 (1992) (intramolecular)
$\text{TiCl}_4, \text{Ti}(\text{O}-i\text{-Pr})_4$	TL 25 3951 (1984) (chiral) JOC 50 2598 (1985) (chiral); 56 6458, 6485 (1991)
cat $\text{Cp}_2\text{Ti}(\text{OTf})_2$	' 4309 (1993) 117 4570 (1995)
ZnBr_2	JACS 110 470 (1988)
cat $(\text{Ph}_3\text{C})\text{ClO}_4$	CL 977 (1985) JACS 117 4570 (1995)
 , Lewis acid	TL 36 8067 (1995)
$\text{ROCH}=\text{CHCH}_2\text{SiMe}_3, \text{TiCl}_4, \text{PPh}_3$	SL 823 (1991) (intramolecular)
$\text{R}'\text{CH}=\text{CHCH}=\text{CHCH}_2\text{SiMe}_3$; cat $\text{BF}_3 \cdot \text{OEt}_2$, Me_3SiI or TiCl_4	TL 21 2049, 3783 (1980); 22 745 (1981) Organomet 1 1651 (1982)
$\text{H}_2\text{C}=\text{CHC}(=\text{CH}_2)\text{CH}_2\text{SiMe}_3, \text{TiCl}_4$ or Me_3SiI	Tetr 39 883 (1983)
$\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{SiMe}_3, \text{TiCl}_4\text{-Ti}(\text{O}-i\text{-Pr})_4$	TL 32 4509 (1991)
$\text{H}_2\text{C}=\text{CHSiMe}_2\text{Cl}, \text{SnCl}_4$	JACS 110 8698 (1988)
$\text{ArSiMe}_2\text{Cl}, \text{SnCl}_4$	JACS 110 8698 (1988)
$\text{RC}\equiv\text{CSiMe}_3, \text{BF}_3 \cdot \text{OEt}_2$, molecular sieves	SL 285 (1995)
$\text{RC}\equiv\text{CSiMe}_3, \text{TiCl}_4$	JACS 105 2904 (1983) (chiral); 112 8042 (1990)
$\text{RC}\equiv\text{CM}$ ($\text{M}=\text{Me}_3\text{Si}, n\text{-Bu}_3\text{Sn}$), Lewis acid?	JACS 108 7116 (1986) (chiral)
$\text{Me}_3\text{SiCN}, \text{BF}_3 \cdot \text{OEt}_2$ ($\text{R}'=\text{CN}$)	TL 22 4279 (1981) Tetr 39 967 (1983) JOC 54 3282 (1989)
Me_3SiCN , cat Me_3SiOTf ($\text{R}'=\text{CN}$)	JACS 115 40 (1993)
Me_3SiCN , cat SnCl_2 ($\text{R}'=\text{CN}$)	TL 22 4279 (1981) Tetr 39 967 (1983)

Me_3SiCN , cat SnCl_4 ($\text{R}' = \text{CN}$)	JACS 115 40 (1993)
Me_3SiCN , cat $n\text{-Bu}_2\text{Sn}(\text{OTf})_2$ ($\text{R}' = \text{CN}$)	JACS 112 901 (1990) (ketals only)
Me_3SiCN , cat $\text{Sc}(\text{OTf})_3$ ($\text{R}' = \text{CN}$)	SL 1077 (1995) (chiral)
Me_3SiCN , TiCl_4 ($\text{R}' = \text{CN}$)	JOC 48 2294 (1983) (chiral); 54 3282 (1989) TL 25 591 (1984) (chiral); 29 2955 (1988) (chiral); 31 2101, 5343 (1990); 34 575 (1993)
$\text{ROCH}=\text{CHCH}_2\text{GeMe}_3$, TiCl_4 , PPh_3	SL 823 (1991) (intramolecular)
$\text{H}_2\text{C}=\text{CHCH}_2\text{SnMe}_3$, $(\text{Et}_2\text{Al})_2\text{SO}_4$	CL 977 (1979)
$\text{H}_2\text{C}=\text{CHCH}_2\text{Sn}(n\text{-Bu})_3$, cat Me_3SiOTf	JACS 115 40 (1993) TL 36 5469 (1995)
$\text{H}_2\text{C}=\text{CHCH}_2\text{Sn}(n\text{-Bu})_3$, TiCl_4	CC 1218 (1987) (chiral) JOC 56 6458, 6485 (1991) JACS 114 10998 (1992)
$\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, $\text{TiCl}_2(\text{O}-i\text{-Pr})_2$	JOC 56 6458, 6485 (1991)
$\text{ROCH}=\text{CHCH}_2\text{SnR}_3$, $\text{TiCl}_3(\text{O}-i\text{-Pr})$	JACS 117 1437 (1995) (intramolecular)
$\text{RC}\equiv\text{CSnR}_3$; $\text{BF}_3\cdot\text{OEt}_2$, SnCl_4 , TiCl_4 or $\text{TiCl}_4\text{-Ti}(\text{O}-i\text{-Pr})_4$	JOC 58 124 (1993)
$n\text{-Bu}_3\text{SnC}\equiv\text{CR}$, TiCl_4	TL 28 4589 (1987)
$n\text{-Bu}_3\text{SnCN}$, Me_3SiOTf ($\text{R}' = \text{CN}$)	TL 36 5469 (1995)
$\text{R}'\text{TiCl}_3$	JOMC 285 83 (1985)
PhCH_2NC , TiCl_4 ($\text{R}' = \text{CONHCH}_2\text{Ph}$)	JOC 54 3282 (1989)
$\text{R}'\text{Cu}$ or $\text{R}'_2\text{CuLi}$, $\text{BF}_3\cdot\text{OEt}_2$	TL 25 3083 (1984) (chiral); 36 7999 (1995) (chiral) Tetr 45 507 (1989)
$\text{R}'_2\text{CuLi}(\text{MgX})$, TiCl_4	TL 25 3947 (1984) (chiral)
R_2BBr ($\text{R} = \text{Me}$, Ph)/ $\text{R}'_2\text{Cu}(\text{CN})\text{Li}_2$	TL 32 5453 (1991) (chiral)

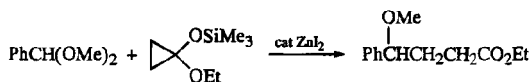
For reactions with enol silanes and Lewis acids, see page 1494, Section 7.2.



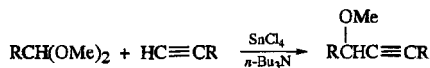
JOC 58 5576 (1993)



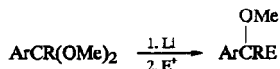
JACS 109 8056 (1987)



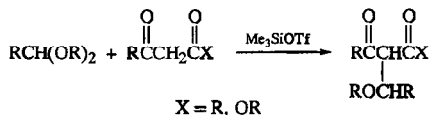
JACS 109 8056 (1987)



CL 2479 (1992)

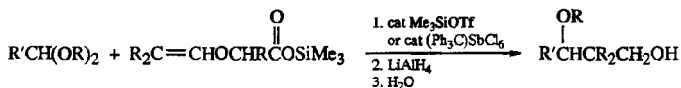
R = H, Ph; E⁺ = D₂O, R'X, RCHO, ClCO₂R

TL 35 6759 (1994)

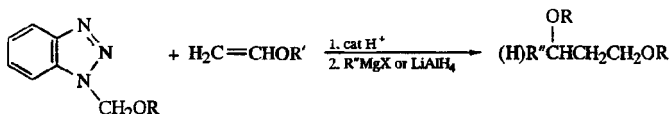


X = R, OR

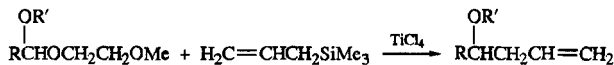
See page 1522, Section 20, and page 1528, Section 22.



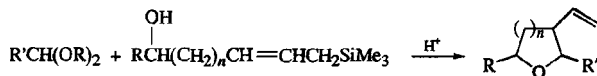
JACS 111 4508 (1989)



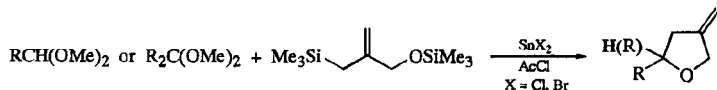
IOC 57 4925 (1992)



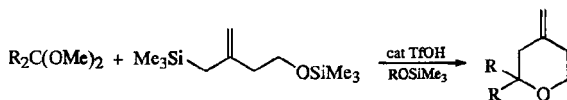
IOC 47 2496 (1982)



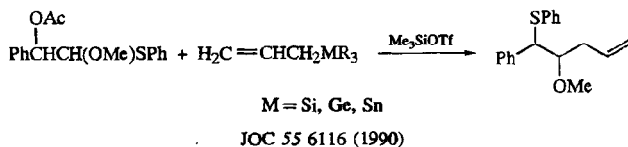
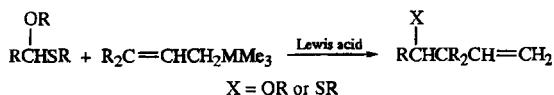
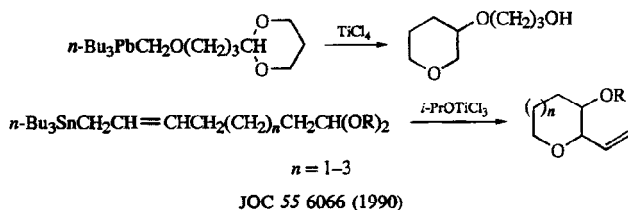
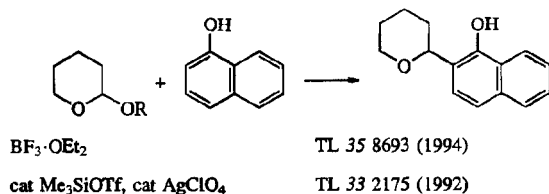
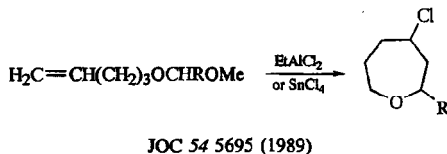
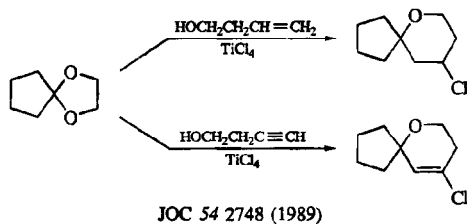
TL 34 6251 (1993) (n = 1); 36 2453 (1995) (n = 2)

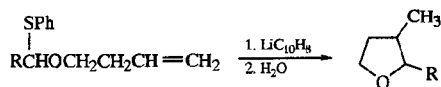


TL 36 5581 (1995)

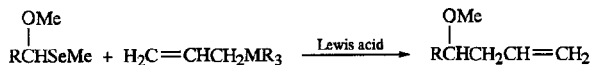


IOC 57 2211 (1992)



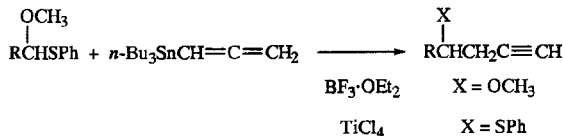


JACS 111 2981 (1989)

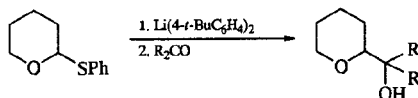


M = Si, Sn

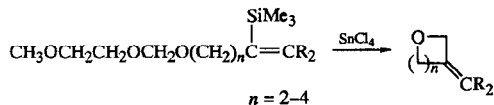
JOC 60 6141 (1995)



TL 28 6299 (1987)

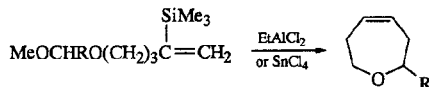


TL 30 3011 (1989)



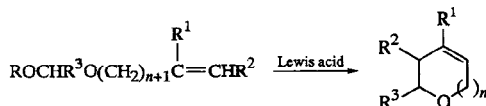
JACS 108 1303 (1986)

JOC 54 5695 (1989)

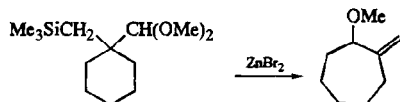


JOC 54 5695 (1989)

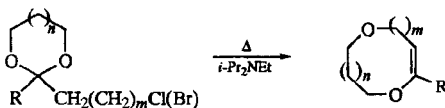
SL 811 (1992)

 $\text{R}^1 = \text{H, SiMe}_3, \text{SPh}; \text{R}^2 = \text{H, Me, } n\text{-Bu}; n = 3, 4$

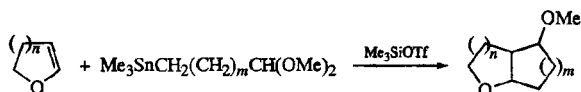
JACS 108 3516 (1986); 110 2248 (1988); 112 4386, 4399 (1990); 115 9305 (1993); 117 5958 (1995)



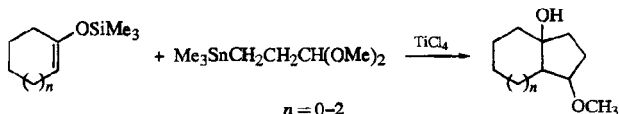
TL 29 1819 (1988)

 $n = 0, 1; m = 2, 3$

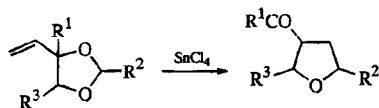
TL 35 49 (1994)

 $n = 1, 2; m = 1-3$

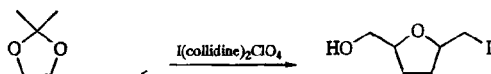
TL 30 3555 (1989)

 $n = 0-2$

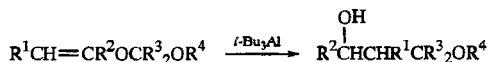
TL 26 3629 (1985)



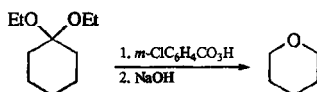
JACS 109 4748 (1987); 113 5354, 5365 (1991)



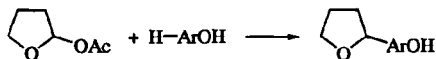
JOC 60 8134 (1995)



JOC 52 5700 (1987)



JOC 50 3009 (1985)

BF₃·OEt₂

TL 31 4629 (1990)

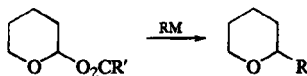
SnCl₄

TL 31 4629 (1990)

Cp₂HfCl₂, AgClO₄

TL 31 4629 (1990)

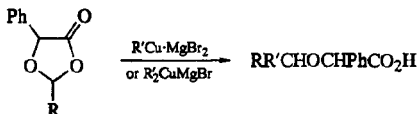
JACS 114 3568 (1992); 116 1004 (1994)

RMRMgX, CuBr·SMe₂ or ZnCl₂

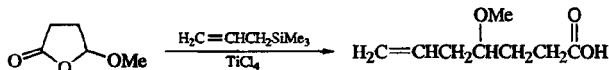
TL 30 6027 (1989)

Me₃SiCH₂CH=CH₂, BF₃·OEt₂

SL 555 (1995)

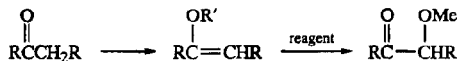


TL 33 5201 (1992)



TL 35 8437 (1994)

2. Aldehydes and Ketones

R'Reagents

Me

F₂, MeOH

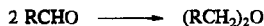
JACS 114 7643 (1992)

SiMe₃(PhIO)_n, BF₃·OEt₂, MeOH

JOC 52 150 (1987)

F₂, MeOH

JACS 114 7643 (1992)

BH₃·py, CF₃CO₂H

CL 415 (1979)

Chem Pharm Bull 27 2405 (1979)

Et₃SiH, CF₃CO₂H

Proc Acad Sci USSR, Chem Sec 179 328 (1968)

JOC 39 2740 (1974)

Et₃SiH, cat (Ph₃C)ClO₄

CL 743 (1985)

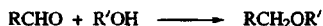
Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$ JOMC 117 129 (1976)

Et_3SiH , cat Me_3SiOTf JOC 52 4314 (1987)



$n\text{-BuSiH}_3$, $\text{CF}_3\text{CO}_2\text{H}$ JOC 39 2740 (1974)

Et_3SiH , cat Me_3SiOTf JOC 52 4314 (1987)



H_2 , cat Pd-C TL 36 4235 (1995)

H_2 , cat PtO_2 , HCl JCS 5598 (1963)

$\text{BH}_3 \cdot \text{py}$, $\text{CF}_3\text{CO}_2\text{H}$ Chem Pharm Bull 27 2405 (1979)

Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$ Proc Acad Sci USSR, Chem Sec 179 328 (1968)

JACS 94 3659 (1972); 114 10971 (1992)

JOC USSR 8 902 (1972)

JOC 59 6142 (1994)

Et_3SiH , H_2SO_4 JACS 94 3659 (1972)



H_2 , cat Pd-C TL 36 4235 (1995)

H_2 , cat $\text{Pd}(\text{OH})_2$ CC 422 (1967)

H_2 , cat PtO_2 , HCl JCS 5598 (1963)

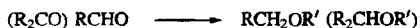
Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$ JACS 94 3659 (1972)

JOC USSR 8 902 (1972)

Et_3SiH , Me_3SiOTf JACS 117 10227 (1995) (intramolecular)

Ph_2MeSiH , Me_3SiOTf JACS 117 10227 (1995) (intramolecular)

$\text{HC}(\text{OEt})_3$, HCl/ Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$ JOC USSR 8 902 (1972)



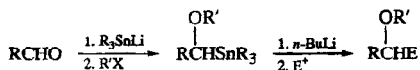
$\text{HC}(\text{OR}')_3$, Nalfion-H/ Et_3SiH , Nalfion-H JOC 51 2826 (1986)

$\text{Me}_3\text{SiOR}'$, cat $(\text{Ph}_3\text{C})\text{ClO}_4$ / Et_3SiH CL 743 (1985)

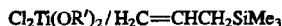
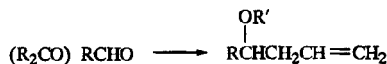
$\text{Me}_3\text{SiOR}'$, cat $\text{Me}_3\text{SiI}/\text{Me}_3\text{SiH}$ JOC 52 4314 (1987)

SL 569 (1992)

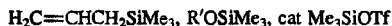
$\text{Me}_3\text{SiOR}'$, Et_3SiH , cat Me_3SiOTf TL 35 4367 (1994)



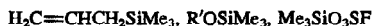
JACS 100 1481 (1978); 106 3376 (1984)



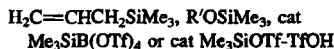
Angew Int 24 765 (1985)



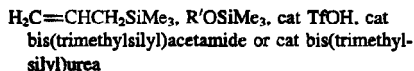
TL 32 4779 (1991); 36 1263 (1995)
JOC 57 5790 (1992); 58 1003 (1993)
JACS 117 10587 (1995)



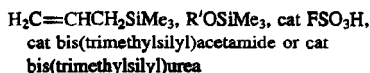
TL 34 995 (1993)



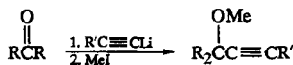
JACS 117 5851 (1995) (chiral)



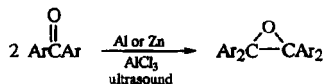
SL 433 (1993)



SL 583 (1993)



Syn 459 (1981)



TL 31 4165 (1990)

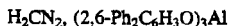


Reviews:

Topics Stereochem 7 93 (1973)

Tetr 36 2531 (1980)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 1, Part 3.2, p 819



SL 521 (1994)



JACS 116 5973 (1994)
TL 36 1731 (1995)



TL 35 2933 (1994)



JACS 84 3782 (1962); 87 1353 (1965); 106 723,
4038 (1984); 109 3353 (1987); 116 9912 (1994)
TL 661 (1962); 169 (1963); 23 5283 (1982); 28 1877
(1987); 30 5425 (1989)
Ber 96 1881 (1963)
JCS C 731 (1970)

Angew Int 12 845 (1973)
Cancer Lett 1 339 (1976)
Heterocycles 8 397 (1977)
JOC 43 3425 (1979); 46 2731 (1981); 51 3393, 5311
(1986); 52 603 (1987); 53 5947 (1988); 54 2777
(1989); 55 501 (1990); 56 3849 (1991); 58 6009
(1993)
Helv 63 1665 (1980)
Syn Commun 12 613 (1982); 15 749 (1985)
CC 1642 (1986)

$$\text{Me}_2\text{S}^+\text{CHAr}^-$$

JOC 46 2731 (1981)

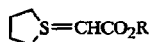
$$\text{Me}_2\text{S}^+\text{CHCH}=\text{CHR}$$

JOC 47 1698 (1982)

$$\text{Me}_2\text{S}^+\text{CHCO}_2^-$$

IOC 35 1600 (1970)

TL 28 2095 (1987)



JOC 55 501 (1990)

$$\text{PhEtS}^+\text{CHR}'$$

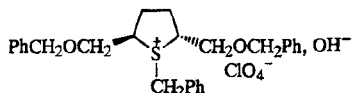
JOC 47 5372 (1982) (intramolecular)

$$[\text{Ar}\overset{+}{\text{S}}(\text{CH}_2\text{R}')_2]\text{O}_3\text{SF}^-, \text{KO-}i\text{-Bu} \text{ (Ar = polymer, R' = H, Me)}$$

TL 203 (1979)

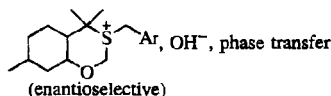
$$\text{R}^+\text{MeCH}_2^- \quad (\text{R} = \text{Me}, n\text{-C}_{12}\text{H}_{25})$$

Helv 63 1665 (1980)



TL 31 35 (1990)

(enantioselective)



JOC 60 3494 (1995)

(enantioselective)

$$\text{Ph}_2\text{S}^+\text{CR}'_2^-$$

TL 2325 (1967)

JOC 59 2324, 5803 (1994)

$$(\text{CH}_3)_2\text{S}^+\text{O}^-\text{CH}_3$$

JACS 84 867 (1962); 87 1353 (1965); 109 1269 (1987); 112 6690 (1990); 114 1438 (1992); 117 5245 (1995)

JOC 33 2188 (1968); 52 4044 (1987); 53 5947 (1988); 54 2209 (1989); 55 501 (1990); 57 86 (1992)

JCS C 731 (1970)

Org Syn Coll Vol 5 755 (1973)

Tetr 49 5067 (1993)


$$\text{ArSOCHClR}', \text{ base} / n\text{-BuLi} / \text{H}_2\text{O} (\text{R}'' = \text{H})$$

TL 27 2379 (1986); 29 313, 2851 (chiral) (1988)

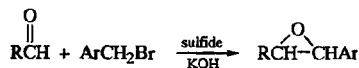
$$\text{PhSO}(=\text{NTs})\text{CH}_2^-$$

JACS 92 5753 (1970)

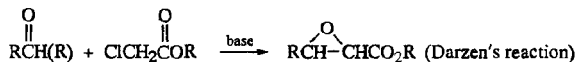
Acct Chem Res 6 341 (1973)

 $\text{NSO(=NTs)CH}_2\text{Na}$	JOC 53 4190 (1988)
$\text{R}\overset{+}{\text{S}}\text{O}(\text{NMe}_2)\bar{\text{C}}\text{R}'_2$	JACS 90 6852 (1968); 92 6594 (1970); 95 7418, 7692 (1973) JOC 38 1793 (1973) Acct Chem Res 6 341 (1973)
$\text{PhS(=NTs)CHR}'\text{Li}$ ($\text{R}' = \text{H, Ph}$)	JOC 44 2065 (1979)
$\text{PhSCH}_2\text{Li} / (\text{Me}_3\text{O})\text{BF}_4 / \text{OH}^-$	JACS 95 3429 (1973)
$\text{MeSCH}_2\text{Li} / \text{MeI} / \text{KO-}i\text{-Bu}$	JOC 50 3988, 5887 (1985); 56 2066 (1991) TL 36 8435 (1995)
$\text{EtSCH=CHCH}_2\text{Ti(O-}i\text{-Pr)}_3 / (\text{Me}_3\text{O})\text{BF}_4 / \text{NaOH}$ ($\text{R}' = \text{CH=CH}_2$, $\text{R}'' = \text{H}$)	JACS 104 7663 (1982)
$\text{EtSCH=CHCH}_2\text{Ti(O-}i\text{-Pr)}_3 / \text{MeO}_3\text{SCF}_3$, 2,6-($t\text{-Bu}$) $_2\text{C}_5\text{H}_3\text{N/Cs}_2\text{CO}_3$ ($\text{R}' = \text{CH=CH}_2$, $\text{R}'' = \text{H}$)	TL 27 5691 (1986)
$\text{LiSCH=CHCH}_2\text{Li}$, $\text{MgBr}_2 / \text{MeI} / \text{NaOH}$ ($\text{R}' = \text{CH=CH}_2$, $\text{R}'' = \text{H}$)	Angew Int 15 437 (1976)
$\text{Ph}_2\text{S} \begin{array}{c} \text{R} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$ ($\text{R} = \text{H, Me}$)	JACS 95 2038, 5311 (1973); 108 4965 (1986); 110 6556, 8591 (1988) JOC 54 3334 (1989)
PhSeMeCH_2^-	Angew Int 20 671 (1981)
$\text{MeSeCH}_2\text{Li} / \text{MeOSO}_2\text{F} / \text{KOH}$	TL 23 4389 (1982)
$\text{MeSeC(Li)Me}_2 / \text{MeOSO}_2\text{F} / \text{KOH}$	CC 564 (1982)
$\text{MeSeCR}'\text{R}''\text{Li} / \text{MeI}$ or $\text{Me}_2\text{SO}_4 / \text{KO-}i\text{-Bu}$	Angew Int 14 700 (1982)
$\text{PhSeO}_2 \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \end{array}$, $\text{KO-}i\text{-Bu}$	TL 29 3265 (1988)
$\text{Ph}_2\text{Te}^+\text{CH}_2^-$	TL 31 4173 (1990)
$i\text{-Bu}_2\text{Te}^+\bar{\text{C}}\text{HCH=CHSiMe}_3$	TL 33 5827 (1992)
$i\text{-Bu}_2\text{Te}^+\bar{\text{C}}\text{HC}\equiv\text{CSiMe}_3$	JOC 57 6598 (1992)
$\text{H}_2\text{C=CHCH}_2\text{Br}$, cat $i\text{-Bu}_2\text{Te}$, Cs_2CO_3 ($\text{R}' = \text{CH=CH}_2$, $\text{R}'' = \text{H}$)	TL 31 7657 (1990)
$\text{Ph}_3\text{As=CHR}'$	JACS 103 1283 (1981) TL 30 179, 2545, 5425 (1989)
$\text{Ph}_3\text{As=CHSPh}$	TL 30 6023 (1989)
$\text{Ph}_3\text{As=CHCH=CH}_2$	JOC 54 3229 (1989)
$\text{Ph}_3\text{As=CHCH=CHCH}_2\text{CH(OEt)}_2$	TL 30 6031 (1989)
$\text{Ph}_3\text{As=CRCH=CHOSiR}_3$	TL 32 2913 (1991)
$(\text{Ph}_3\text{AsCH}_2\text{CH=CHCH}_2\text{OH})\text{X}$, $\text{KF}\cdot\text{Al}_2\text{O}_3$	TL 32 3999 (1991)
$(\text{Ph}_3\text{AsCH}_2\text{CH}_2\text{OH})\text{Br}$, KOH	TL 29 5295 (1988)

$\text{CH}_3\text{CH}=\text{CBrCO}_2\text{Et}$, LDA ($\text{R}' = \text{CH}=\text{CH}_2$, $\text{R}'' = \text{CO}_2\text{Et}$)	JOC 51 4746 (1986)
$\text{R}_3\text{SiOCH}_2\text{CH}=\text{C}(\text{Br})\text{CO}_2\text{R}$, LDA ($\text{R}' = \text{CH}=\text{CHOSiR}_3$, $\text{R}'' = \text{CO}_2\text{R}$)	JOC 56 4598 (1991)
$\text{LiCH}_2\text{CH}=\text{C}(\text{OEt})\text{N} \begin{array}{c} \diagup \text{N} \diagdown \\ \quad \\ \text{C}_6\text{H}_4 \end{array} \text{N}/\text{ZnBr}_2$ ($\text{R}' = \text{CH}=\text{CH}_2$, $\text{R}'' = \text{OEt}$)	JOC 60 6, 7597 (1995)
$\text{py}-\text{CHR}'\text{Cl}$, LDA ($\text{R}'' = \text{py}$)	TL 35 3175 (1994)
$\text{Cl}_2\text{CHCO}_2\text{Me}$, cat $\text{Ni}(\text{bipy})_3(\text{BF}_4)_2$, electrolysis ($\text{R}' = \text{CO}_2\text{Me}$)	JOC 56 2018 (1991)
H_2CCl_2 , MeLi	TL 27 795 (1986); 34 3173 (1993) SL 491 (1994) JOC 60 6696 (1995)
H_2CBr_2 , Li	CC 1047 (1969) Tetr 27 6109 (1971)
H_2CBr_2 , Li(Hg)	Tetr 27 6109 (1971)
H_2CBr_2 , MeLi	JOC 60 6696 (1995)
H_2CBr_2 , <i>n</i> -BuLi	Tetr 27 6109 (1971); 49 5067 (1993) SL 631 (1991)
H_2CBr_2 , <i>sec</i> -BuLi, LiBr	TL 25 835 (1984)
H_2Cl_2 , MeLi	JOC 60 6696 (1995)
$\text{ClCH}_2\text{SiMe}_3$, CsF ($\text{R}' = \text{R}'' = \text{H}$)	JOC 56 3908 (1991)
ArCHBrSiMe_3 , CsF ($\text{R}' = \text{Ar}$, $\text{R}'' = \text{H}$)	JOC 56 3908 (1991)
$\text{ClCH}=\text{CHCH}_2\text{ZnCl}/\text{KOEt}$ ($\text{R}' = \text{CH}=\text{CH}_2$)	TL 34 3145 (1993)



JOC 54 4222 (1989) (chiral)



Org Rxs 5 413 (1949) (review)

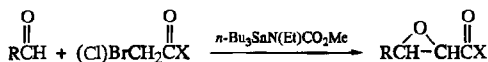
JACS 82 5459 (1960)

J Fluorine Chem 17 565 (1981)

JOC 54 5054 (1989); 56 2427 (1991); 57 851 (1992)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2,
Part 1.13, p 409 (review)

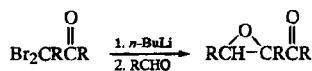
TL 34 2753 (1993) (intramolecular); 35 5205 (1994)



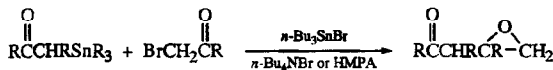
X = R, OR

SL 490 (1990)

JOC 57 6909 (1992)

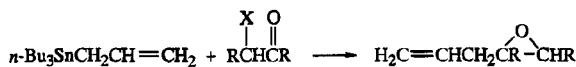


SL 1071 (1995)



JOC 48 4629 (1983), 59 4386 (1994)

JCS Perkin I 859 (1993)



X = Cl, Br

 $n\text{-Bu}_2\text{SnX}_2$, HMPA

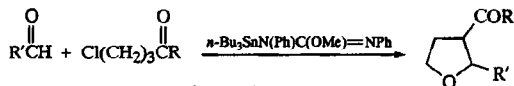
SL 555 (1991)

cat $\text{Pd}(\text{PPh}_3)_4$

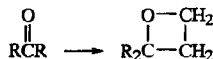
CL 795 (1978)

cat $\text{PhCH}_2\text{PdCl}(\text{PPh}_3)_2$

JOC 48 4829 (1983)



JOC 57 6909 (1992)

 $\text{H}_2\text{C}=\text{CH}_2$, hv

See page 912, Section 4.

 $\text{F}_2\text{C}=\text{CF}_2$, $\text{AlCl}_x\text{F}_{3-x}$

JOC 60 3419 (1995)

 $\text{LiCH}_2\text{CO}_2\text{R}$ / LiAlH_4 / $p\text{-TsCl}$ / $\text{KO}-t\text{-Bu}$

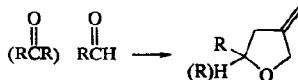
TL 36 8435 (1995)

 $\text{MeSO}(\text{=NTs})\text{CH}_2\text{Na}$

JACS 101 6135 (1979)

 $\text{O} \begin{array}{c} \diagup \diagdown \end{array} \text{NSO}(\text{=NTs})\text{CH}_2\text{Na}$

JOC 53 4190 (1988)

 $\text{R}_2\text{BCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{OPh}$ / $n\text{-BuLi}$ / Pd catalyst

TL 34 4655 (1993)

 $\text{Me}_3\text{SiCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{Cl}$, $\text{BF}_3 \cdot \text{OEt}_2$ / DBU , LiClO_4

SL 119 (1993)

$\text{Me}_3\text{SiCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{OAc}$, cat $\text{Pd}(\text{OAc})_2$,
cat $(i\text{-PrO})_3\text{P}$ JACS 111 5902 (1989)

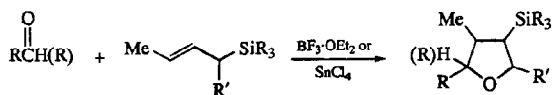
$\text{Me}_3\text{SiCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{OAc}$, cat $n\text{-Bu}_3\text{SnOAc}$ or
 Me_3SnOAc , cat $\text{Pd}(\text{OAc})_2$, cat PPh_3 TL 27 5971 (1986)
JACS 111 5902 (1989); 112 408 (1990); 113
9007 (1991)

$\text{Me}_3\text{SiCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{OAc}$, cat $\text{In}(\text{acac})_3$, cat
 $\text{Pd}(\text{OAc})_2$ - $i\text{-Bu}_2\text{AlH}$ - PPh_3 JACS 114 7903 (1992)

$\text{Me}_3\text{SiCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{O}_2\text{CR}$, cat $\text{In}(\text{acac})_3$, cat
 $\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3$, cat PPh_3 TL 34 7183 (1993)

$\text{R}'_3\text{SnCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{OAc}$, cat $\text{Pd}(\text{OAc})_2$,
cat PPh_3 JACS 107 1778, 8277 (1985); 112 408 (1990)

$\text{BrZnCH}_2\text{C}(\text{=CH}_2)\text{CH}_2\text{OPh}$ / cat $\text{Pd}(\text{PPh}_3)_4$ TL 29 3579 (1988)

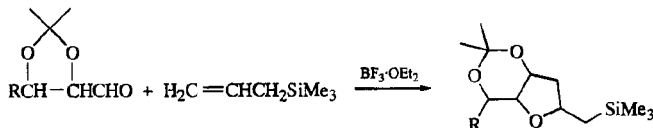


JACS 113 9868 (1991)

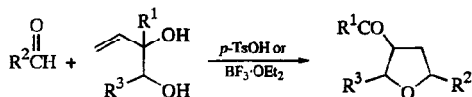
JOC 58 809 (1993)

TL 35 8401 (1994)

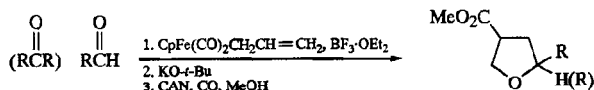
CL 627 (1994)



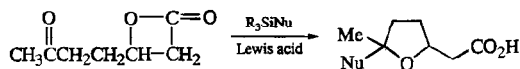
TL 31 5909 (1990); 36 5789 (1995)



JACS 113 5354, 5365, 5378 (1991)

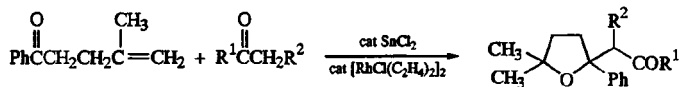


TL 35 7889 (1994)

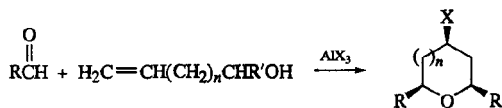


Nu = H, $\text{CH}_2\text{CH}=\text{CH}_2$, CN

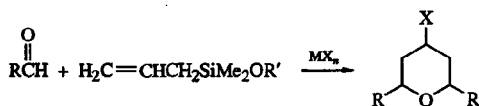
TL 34 6997 (1993)



TL 34 7971 (1993)

 $n = 1, 2; \text{X} = \text{Cl, Br}$

JOC 53 911 (1988)

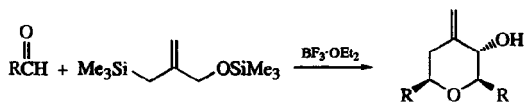
 $\text{MX} = \text{BF}_3, \text{AlCl}_3, \text{SnCl}_4$

JOC 54 5768 (1989)

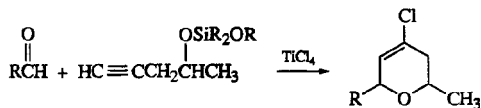


TL 32 4738 (1991); 33 1799 (1992)

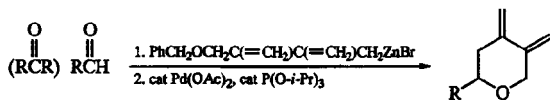
JOC 57 2211 (1992)



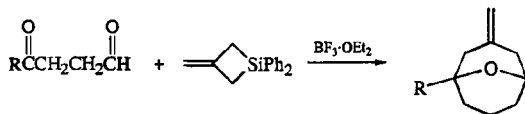
TL 34 6595 (1993)



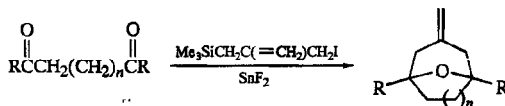
TL 30 4065 (1989)



TL 30 5497 (1989)



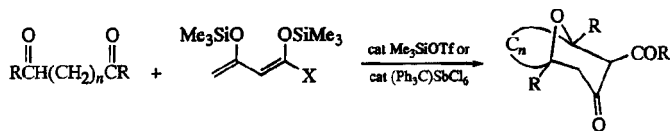
TL 36 8067 (1995)

 $n = 1, 2$

JACS 109 6877 (1987)

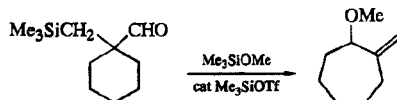
TL 30 2351 (1989)

JOC 60 4559 (1995)

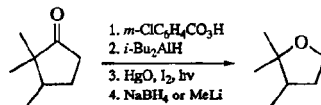
 $n = 2, 3; \text{X} = \text{R, OMe}$

JACS 115 830 (1993)

JOC 59 7148 (1994); 60 130, 4559, 4845, 8382 (1995)



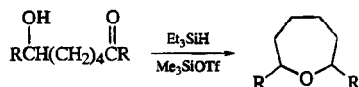
TL 29 1819 (1988)



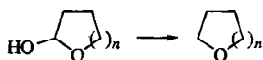
TL 25 3995 (1984)

JOC 50 2489 (1985); 55 2170 (1990)

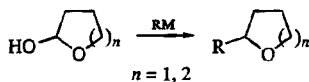
3. Lactols



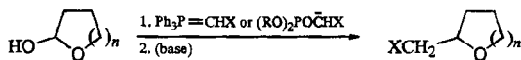
JACS 111 4136 (1989)

Reagents

Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$	$\frac{n}{2}$	CC 1568 (1986) JOC 55 1105 (1990)
Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$	1, 2	JOC 46 2417 (1981); 53 2450, 4282 (1988); 54 610 (1989); 57 2154 (1992) JACS 104 4796 (1982); 111 6666 (1989); 114 4128 (1992) Carbohydr Res 128 C9 (1984) CC 1512 (1985)

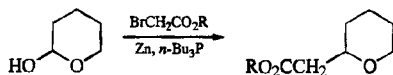
RM

R_3Al (R = Me, Et), $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{SnBr}_2$, $n\text{-Bu}_2\text{Sn}(\text{CH}=\text{CH}_2)_2$ or R_2Zn (R = Me, Et, Ph); $\text{BF}_3 \cdot \text{OEt}_2$	TL 28 6339 (1987)
$\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$, $\text{BF}_3 \cdot \text{OEt}_2$	JACS 104 4976 (1982) Angew Int 25 556 (1986) JOC 53 2450 (1988) SL 40 (1990)
$\text{RC}\equiv\text{CSiMe}_3$, $\text{BF}_3 \cdot \text{OEt}_2$	JOC 53 2450 (1988)
$\text{HC}\equiv\text{CCH}_2\text{SiMe}_3$, $\text{BF}_3 \cdot \text{OEt}_2$ (allene)	JOC 53 2450 (1988) SL 40 (1990)
$\text{HC}\equiv\text{CCH}_2\text{SiMe}_3$, Me_3SiOTf (allene)	JOC 57 490 (1992)
$\text{Me}_3\text{SiBr}/\text{ArMgX}$	JOC 57 7046 (1992)
Me_3SiCN , $\text{BF}_3 \cdot \text{OEt}_2$ (R = CN)	Angew Int 25 556 (1986) JOC 53 2450 (1988)
$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$, $\text{BF}_3 \cdot \text{OEt}_2$	JOC 56 7237 (1991)

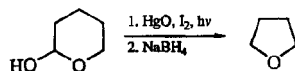


$n = 1, 2$; X = COR, CO₂R, CN, SO₂R

JACS 97 4602 (1975)
JOC 47 5381 (1982); 49 522 (1984); 53 1432 (1988); 57 2888 (1992)
CC 297 (1982); 1292 (1985)
TL 25 5697 (1984); 28 5047 (1987); 29 693 (1988); 34 7541 (1993)
JCS Perkin I 1281 (1989)

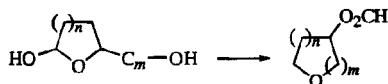


Carbohydr Res 224 301 (1992)



TL 32 5999 (1991)

IOC 60 3052 (1995)

Reagent(s)n, mPhIO, I₂

1, 1; 1, 2; 2, 1

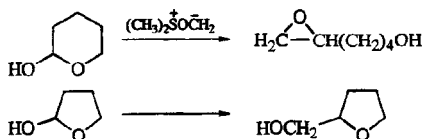
TL 34 7331 (1993)

JACS 115 8865 (1993)

Ph₂Se(OH)OAc, I₂

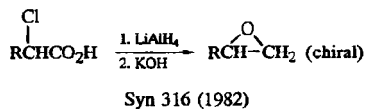
1, 1; 1, 2; 2, 1

TL 35 2049 (1994)

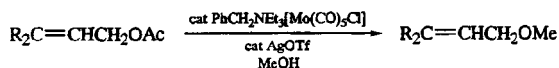


TL 33 5067 (1992)

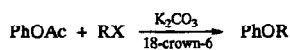
4. Carboxylic Acids



5. Esters and Lactones

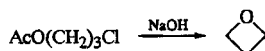


TL 36 6351 (1995)

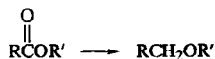


R = 1° alkyl, allylic, benzylic

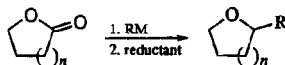
CC 815 (1982)



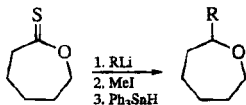
SL 783 (1991)



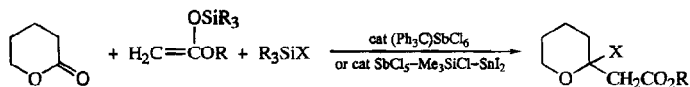
H_2 , cat Pt oxide (5-alkanolides)	Chem Ind 975 (1964)
BH_3	JOC 26 1685, 4553 (1961); 27 2127 (1962); 36 3485 (1971) Can J Chem 44 1097 (1966)
<i>i</i> -Bu ₂ AlH/Et ₃ SiH, BF ₃ ·OEt ₂ (4- and 5-alkanolides)	JOC 46 2417 (1981) JACS 117 211 (1995)
LiAlH ₄ , BF ₃ ·OEt ₂	JOC 25 875 (1960) Tetr 18 953 (1962)
LiAlH ₄ , AlCl ₃ (5- and 6-alkanolides)	Chem Ind 230 (1977)
HSiCl ₃ , hv	JACS 91 4587 (1969) JOC 37 76, 4349 (1972); 38 795 (1973); 39 2470 (1974); 40 3885 (1975) BCSJ 47 932 (1974)
(ArPS ₂) ₂ S, Raney Ni	JOC 46 831 (1981); 57 2818 (1992)



<u>RM</u>	<u>n</u>	<u>Reductant</u>	
MeLi	2	Et ₃ SiH, CF ₃ CO ₂ H	CC 1568 (1986)
ArCH ₂ Li	2	PhSH, BF ₃ ·OEt ₂ / <i>n</i> -Bu ₃ SnH	JOC 59 737 (1994)
LiCH ₂ CO ₂ Et, H ₂ C=CHCH ₂ MgBr	2	Et ₃ SiH, BF ₃ ·OEt ₂	JACS 104 4976 (1982)
ArLi	1, 2	Et ₃ SiH, BF ₃ ·OEt ₂	JOC 54 610 (1989)
ArLi(MgX)	2	NaBH ₃ CN	JOC 58 3191 (1993)
ArLi(MgX), H ₂ C=CHMgBr	2	Et ₃ SiH, BF ₃ ·OEt ₂	JOC 53 752 (1988)
Li	1, 2	Et ₃ SiH, Me ₃ SiOTf	TL 34 7319 (1993) JOC 59 6404 (1994)
RC≡CLi, Li	1, 2	Et ₃ SiH, BF ₃ ·OEt ₂	TL 30 5713 (1989) JOC 57 1065 (1992) SL 705 (1994)
ArMgX	1, 2	Et ₃ SiH, CF ₃ CO ₂ H	CC 1568 (1986)

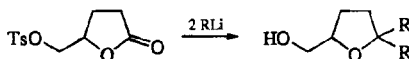


JACS 109 2504 (1987); 112 6263 (1990)



X = H, CH₂Ph, CH₂CH=CH₂, CN

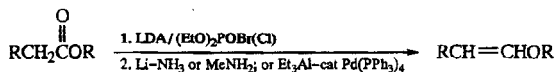
BCSJ 63 1898 (1990)



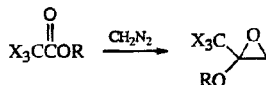
TL 35 7467 (1994)



See page 341, Section 16.

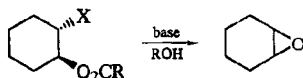


JOC 52 2303 (1987); 55 1670 (1990)



X = F, Cl

JOC 53 3321 (1988)



X

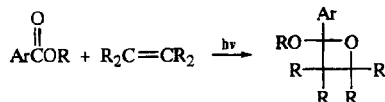
halogen

TL 29 143, 277 (1988); 32 1987 (1991)

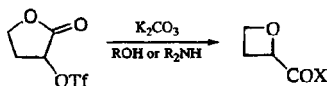
JACS 114 4453 (1992)

OTs

TL 29 4221 (1988)



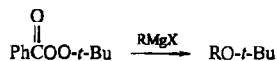
JOC 54 135, 140 (1989)



X = OR, NR₂

TL 28 4741 (1987); 29 1449 (1988); 31 4787, 6927, 6931 (1990)

6. Peresters



R = alkyl, aryl

JACS 81 4230 (1959)

Org Syn 43 55 (1963)

Org Syn Coll Vol 5 924 (1973)

7. Ortho Esters and Related Compounds



RM

RMgX (R = alkyl, allylic, vinylic, alkynyl)

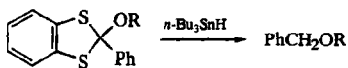
Bull Soc Chim Belg 92 215 (1983)

PhMgBr

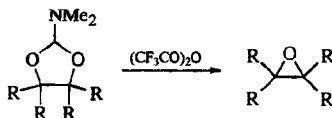
Ber 103 643 (1970)

RCH=CR'CH₂Al_{2/3}Br

JOMC 222 1 (1981)

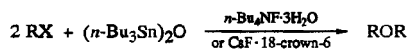


TL 31 3051 (1990)

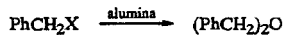


TL 30 6797 (1989)

5. MISCELLANEOUS REACTIONS

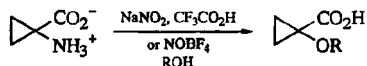


JACS 110 7737 (1988)

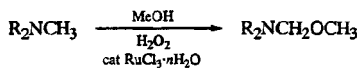


X = Cl, Br

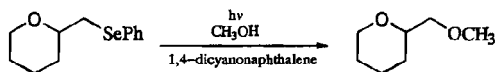
TL 35 6211 (1994)



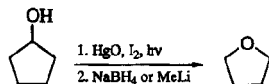
JACS 112 6388 (1990)



TL 33 6991 (1992)



JACS 112 5650 (1990)



CL 55 (1983)

JOC 49 3753 (1984); 60 3052 (1995)

ALCOHOLS AND PHENOLS

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- "The Chemistry of the Hydroxyl Group," Parts 1 and 2, Ed. S. Patai, Interscience, New York (1971)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/1c, Parts I and II, G. Thieme, Stuttgart (1976) (phenols)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/1a, Parts I and II, G. Thieme, Stuttgart (1979 and 1980, respectively) (alcohols)
- "Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues," Parts 1 and 2, Ed. S. Patai, J. Wiley, Chichester, U. K. (1980)
- Syn 501 (1981) (preparation of acetals from alcohols or oxiranes and carbonyl compounds)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/1b, Part III, G. Thieme, Stuttgart (1984) (alcohols)
- "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 6, Part 1.1, p 1
- "The Chemistry of Hydroxyl, Ether and Peroxide Groups," Ed. S. Patai, Supplement E2, J. Wiley, Chichester, U. K. (1993)

1. RESOLUTION

1.1. Deracemization

Appl Environ Microbiol 53 519 (1987)
Agric Biol Chem 54 1819 (1990)
Biocatalysis 5 249 (1992)
TL 36 6263 (1995)

1.2. Resolution of alcohols by lipase-catalyzed esterification

TL 29 5133 (1988)

1.3. Resolution of alcohols by lipase-catalyzed transesterification

JACS 107 7072 (1985); 110 7200 (1988); 112 7434 (1990); 113 3166, 6129 (1991); 114 8349 (1992)
JOC 52 256 (1987); 53 2374 (1988); 54 2453, 2646 (1989); 55 1138, 3377, 4237, 6214 (1990); 56
1966, 2050 (1991); 57 3231, 3867, 4323 (1992); 58 1003, 1570, 2173, 5000 (1993); 59 251, 388,
1751, 6018 (1994)
TL 28 1647 (1987); 29 2455 (1988); 32 4085, 5159, 5497 (1991); 33 1201 (1992); 34 305 (1,2 diols),
1367, 2307, 6581 (1993); 35 4915, 5205, 6975, 7973 (1994); 36 1675, 3715, 6253 (1995)
SL 310 (1991); 410, 813 (1992); 108, 491 (1993); 754, 929 (1994)
See also page 1969, Section 20.

1.4. Resolution of alcohols by oxidation

JOC 59 924 (1994)

1.5. Resolution of allylic alcohols

Sharpless epoxidation

JACS 103 6237 (1981); 109 5765 (1987)
JOC 48 5093 (1983); 54 4016 (1989); 55 5324 (1990); 56
240, 6966 (1991); 59 1444, 4311 (1994)
CC 1323, 1732 (1986)
TL 28 2033, 6351 (1987); 30 7083 (1989); 32 5789 (1991)
CL 1523 (1987)
SL 117 (1992); 293 (1993)

hydrogenation

JOC 53 708 (1988)
TL 34 7359 (1993)

Cu complexation

TL 35 169 (1994)

oxidation

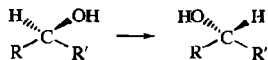
TL 36 2243 (1995)

1.6. Resolution of 2,3-epoxy alcohols**TL 32 3547 (1991)**

2. ALCOHOL TRANSPOSITION

Epimerization of alcohols

Na	Bull Soc Chim Belg 70 767 (1961)
LiAlH ₄ , AlCl ₃	JACS 82 1367 (1960)
Al(O- <i>i</i> -Pr) ₃ , <i>i</i> -PrOH, acetone	JACS 73 5824 (1951); 79 5992 (1957); 87 5031 (1965); 88 3327 (1966)
	JOC 26 3504 (1961); 28 1079 (1963)
	Bull Soc Chim Belg 70 767 (1961)
Raney Ni	Bull Soc Chim Belg 70 767 (1961)
	JACS 87 5031 (1965); 88 3327 (1966)
Ni	JCS 2165 (1956)
NaH, NaOCMe ₂ CH ₂ CH ₂ CMe ₂ ONa, Ni(OAc) ₂ , (MgBr ₂)	TL 29 1383 (1988)
	JOC 55 5916 (1990)
Pt	JCS 2165 (1956)

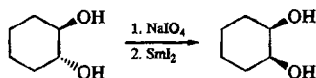


TsCl / (<i>n</i> -Bu ₄ N)OAc / LiAlH ₄	JCS C 1605 (1969)
TsCl / (Et ₄ N)OAc[O ₂ CH] / saponify	TL 3265, 3269 (1972)
TsCl / NaO ₂ CPh / K ₂ CO ₃	JACS 96 5876 (1974)
<i>p</i> -ClC ₆ H ₄ SO ₂ Cl / KO ₂ CH(OAc) / saponify	Ann 901 (1974)
TsCl / DMF / saponify	JACS 80 2906 (1958)
<i>p</i> -XC ₆ H ₄ SO ₂ Cl (X = Cl, Me) / KNO ₂	Ann 901 (1974)
	Syn 292 (1980)
TsCl or MsCl / (<i>n</i> -Bu ₄ N)NO ₃ / reduction	TL 26 3369 (1985)
MsCl / KOH	JACS 107 2138 (1985)
MsCl / KO ₂	TL 3183 (1975)

MsCl, Et ₃ N/CsO ₂ CEt, DMF/hydrolysis	JOC 46 4321 (1981)
mesylation/CsOAc, 18-crown-6/hydrolysis	CL 1555 (1984)
Ms ₂ O, Et ₃ N/CsOAc, DMF/K ₂ CO ₃ , MeOH	TL 28 503 (1987)
Tf ₂ O, py/KNO ₂ , 18-crown-6	TL 34 8029 (1993)
PhCOCl/Al ₂ O ₃	Helv 42 2177 (1959)
RCO ₂ H, EtO ₂ CN=NCNCO ₂ Et, R ₃ P/base	BCSI 40 2380 (1967); 44 3427 (1971); 49 510 (1976)
	TL 1619 (1973); 27 3535 (1986); 28 723, 1143, 3151 (1987); 29 4237 (1988); 32 3017 (1991); 33 4317 (1992)
	Helv 59 2100 (1976); 60 417 (1977)
	Angew Int 18 958 (1979)
	Syn 1 (1981) (review)
	JOC 48 5083 (1983); 50 2981 (1985); 52 3468, 3883, 4235 (1987); 56 67 (1991); 58 385, 832 (1993)
	JACS 107 4339 (1985); 109 4690 (1987)
HOAc, (Me ₃ CCH ₂ O) ₂ CHNMe ₂ /saponify	Ann 821 (1974)
CrO ₃ , H ₂ SO ₄ /NaBH ₄	JACS 110 1985 (1988)



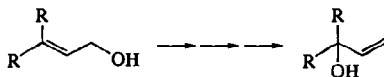
TL 26 607 (1985)



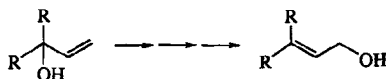
TL 32 1125 (1991)



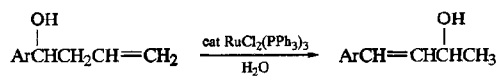
TL 35 331 (1994)



See page 227, Section 3.



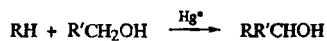
See page 227, Section 3.



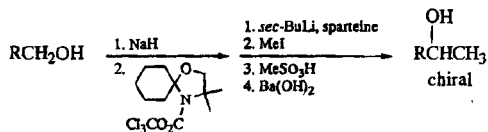
See page 227, Section 3.

3. SUBSTITUTION

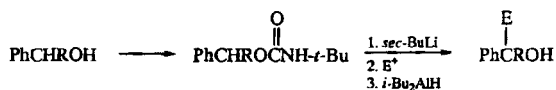
1. Hydrogen Substitution



JACS 111 2946 (1989)

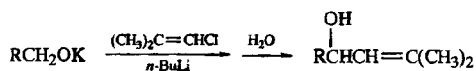


Angew Int 29 1422 (1990)



$\text{E}^+ = \text{RX}, \text{RCHO}, \text{Me}_3\text{SiCl}$

TL 30 5413 (1989)



JACS 107 2189 (1985)

JOC 53 3089 (1988)



JACS 105 2771 (1983)

2. Halide and Sulfonate Substitution



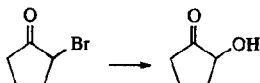
H ₂ O	JOC 52 4592 (1987) (2° benzylic bromide)
H ₂ O, HMPA or NMP	JOC 48 1360 (1983) (1°, 2° alkyl bromide and iodide; 2° alkyl tosylate; allylic chloride)
H ₂ O, 2-pyrrolidinone	JOC 60 2059 (1995) (R _f -CH ₂ CH ₂ I)
H ₂ SO ₄ , SO ₃ /H ₂ O	JOC 59 6804 (1994) (1° alkyl iodide)
AgNO ₃ , H ₂ O	JACS 110 8153 (1988) (1°, 2° benzylic)
Ag ₂ O, H ₂ O	JOC 59 7108 (1994) (2° alkyl chloride)
LiOH, H ₂ O	JOC 60 1160 (1995) (1° alkyl bromide)
NaOH, (<i>n</i> -Bu ₄ N)HSO ₄	JOC 56 7350 (1991) (aryl fluoride)
Al ₂ O ₃ , H ₂ O	CC 1136 (1987) (2° alkyl chloride)
CaCO ₃ , H ₂ O	JOC 51 3762 (1986); 59 7876 (1994) (both 1° benzylic bromide); 60 1160 (1995) (1° alkyl bromide)
polymer-supported carbonate	Syn 793 (1981) (1° alkyl chloride, bromide, iodide; 1° allylic bromide; 1° benzylic chloride, bromide)
(<i>n</i> -Bu ₄ N)OAc/LiAlH ₄	JCS C 1605 (1969) (2° alkyl tosylates)
(<i>n</i> -Bu ₃ Sn) ₂ O; AgNO ₃ , AgOTf or Ag ₂ O/H ₂ O or SiO ₂	TL 30 279 (1989) (1° alkyl bromide or iodide)
KO ₂ , 18-crown-6/H ₂ O	TL 3183 (1975) (1° alkyl, allylic, benzylic bromides; 2° alkyl tosylate; 2° allylic mesylate); 31 7509 (1990) (2° allylic bromide) JOC 58 385 (1993) (2° alkyl triflate)
Li or Mg/O ₂ or <i>t</i> -BuO ₂ Li	JOC 41 1459 (1976) (2° cyclopropyl bromide)
Li/MoO ₅ ·py·HMPA	JOMC 59 293 (1973) (1° alkyl lithium)
<i>n</i> -BuLi/B(OMe) ₃ /H ₂ O	TL 32 4879 (1991) (aryl)
<i>n</i> -BuLi/B(OMe) ₃ /NMO	SL 931 (1995) (aryl)
Mg/MoO ₅ ·py·HMPA	JOC 42 1479 (1977) (aryl bromides) Austral J Chem 31 2091 (1978) (1°, 2°, 3° alkyl bromides; aryl bromides)
Mg, B ₂ H ₆ /H ₂ O ₂ , NaOH	TL 29 3513 (1988) (aryl bromide)
Ph ₂ SbSbPh ₂ , hν/H ₂ O ₂ , NaOH	JACS 113 8177 (1991) (1° alkyl iodides)
air, <i>n</i> -Bu ₃ SnH/NaBH ₄	JACS 113 8980 (1991) (1°, 2°, 3° alkyl iodides; 1°, 2° allylic bromides)

O_2 , $n\text{-Bu}_3\text{SnH}$

TL 35 8163 (1994) (2° alkyl iodide)

 $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$

JACS 100 4888 (1978) (1° alkyl iodide)

 H_2O , NMP

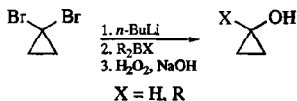
JOC 48 1360 (1983)

 $NaOH$, DMF

JOC 47 4024 (1982)

 N_2H_4 , H_2O/H_2SO_4 , MeOH

JOC 32 3723 (1967)



JOC 50 2401 (1985)

 $n\text{-Bu}_3\text{SnCH}_2\text{OH}$, 2 $n\text{-BuLi}/H_2O$

Angew Int 15 438 (1978)

Ber 113 1290 (1980)

 $(i\text{-PrO})_2\text{MeSiCH}_2\text{MgCl}$; Cu , Ni or Pd catalyst/ H_2O_2
or CH_3CO_3H

JOC 48 2120 (1983)

 $(i\text{-PrO})_2\text{MeSiCH}_2\text{MgCl}$, cat Li_2CuCl_4/KHF_2 , H_2O_2

JACS 108 6389 (1986)

 $(\text{Mes})_2\text{BCH}_2\text{Li}/[O]$

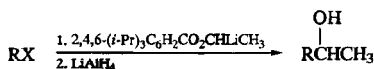
Chem Soc Rev 11 191 (1982)

 $\text{BCH}_2\text{Li}/H_2O_2$, $NaOH$

JACS 94 6854 (1972)

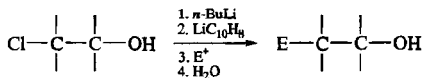
2,4,6- $(i\text{-Pr})_3\text{C}_6\text{H}_2\text{CO}_2\text{CH}_2\text{Li}/\text{LiAlH}_4$

JACS 99 5213 (1977)



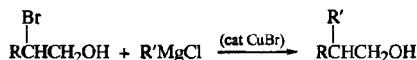
JOC 43 4255 (1978)

For analogous conversions, see page 1125, Section 9.

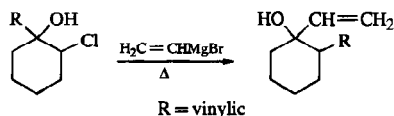
 $E^+ = D_2O$, RX , $RCHO$, R_2CO , CO_2 , O_2 , Me_2S_2

CC 1153 (1982)

JCS Perkin I 3019 (1983)

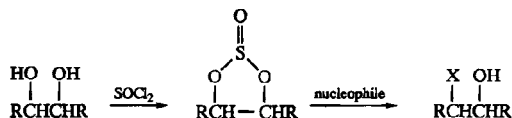
 $R' = \text{allyl, vinyl, aryl}$

BSCF II 289 (1980)



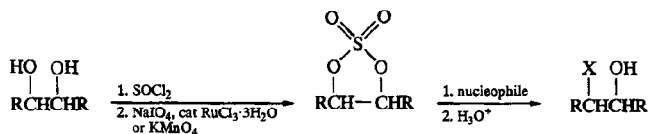
JACS 112 8478 (1990)

3. Cyclic Sulfite, Sulfate and Thiocarbonate Substitution



Review: Syn 1035 (1992)

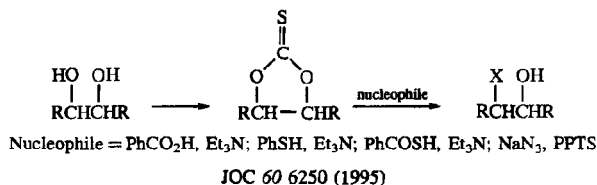
<u>X</u>	<u>Nucleophile</u>	
Cl, Br	LiX	TL 32 3155 (1991)
OAc	NaOAc	TL 32 3155 (1991)
SAr	ArSH	JOC 60 5983 (1995)
SCN	NH ₄ SCN	TL 32 3155 (1991)
N ₃	LiN ₃	TL 31 4317 (1990)
		CC 95 (1991)
	NaN ₃	TL 26 6343 (1985); 32 3155 (1991)



Review: Syn 1035 (1992)

<u>X</u>	<u>Nucleophile</u>	
H	NaBH ₃ CN	JACS 110 7538 (1988)
F	(Me ₄ N)F	JOC 48 3507 (1983); 55 1211 (1990)
	(Et ₄ N)F	JACS 110 7538 (1988)
	(n-Bu ₄ N)F	CL 1689 (1989)
Br	(Me ₄ N)Br	JOC 48 3507 (1983)
I	(n-Bu ₄ N)I	JCS Perkin I 2017 (1994)
OAr	KOAr	J Heterocyclic Chem 9 891 (1972)
		JOC 55 1211 (1990)
OAc	(n-Bu ₄ N)OAc	Tetr Asym 5 1353 (1994)

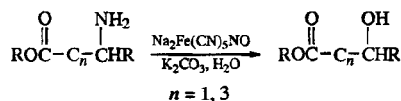
O_2CPh	$(NH_4)_2O_2CPh$	JACS 110 7538 (1988)
	$PhCO_2H, K_2CO_3$	TL 30 655 (1989)
		J Heterocyclic Chem 9 891 (1972)
SPh	NaSPh	J Heterocyclic Chem 9 891 (1972)
SCN	NH_4SCN	JACS 110 7538 (1988)
SePh	NaSePh	JCS Perkin I 2017 (1994)
	$NaBH_4, (PhSe)_2$	CC 995 (1993)
NHR	RNH_2	J Heterocyclic Chem 9 891 (1972)
		TL 30 2623 (1989)
N_3	LiN_3	TL 30 655, 2623 (1989)
		JOC 60 5332 (1995)
	NaN_3	JACS 110 7538 (1988)
		TL 31 2337 (1990)
NO_3	$(n-Bu_4N)NO_3$	JACS 110 7538 (1988)
R	$RMgX, cat Li_2CuCl_4$	JACS 110 7538 (1988)
Ar	$ArLi$	J Heterocyclic Chem 9 891 (1972)
$C\equiv CR$	$LiC\equiv CR$	J Heterocyclic Chem 9 891 (1972)
$CH(CO_2R)_2$	$NaCH(CO_2R)_2$	J Heterocyclic Chem 9 891 (1972)



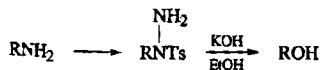
4. Nitrogen Substitution



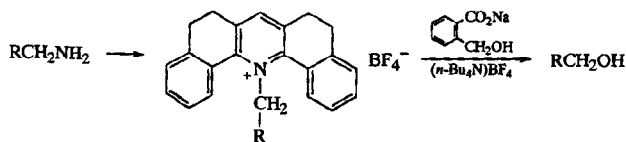
$N_2O_4/Zn, HOAc$	JCS Perkin I 1114 (1977)
$NaNO_2, HOAc, H_2O$	Tetr 28 4131 (1972)
$NaNO_2, HCl, H_2O$	JOC 53 3621 (1988)
	JACS 110 940 (1988)
$NaNO_3, H_2SO_4$	Tetr 35 1601 (1979)
	TL 36 6965 (1995)
	JOC 60 5303 (1995)



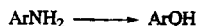
JOC 51 3913 (1986)



TL 33 7465 (1992)



JCS Perkin I 1492 (1981)

NaHSO₃/NaOH/HCl

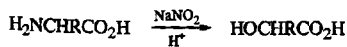
JACS 83 5015 (1961)

NaNO₂, H₂SO₄/H₂O, H₂SO₄, Na₂SO₄

Org Syn Coll Vol 3 130 (1955)

DMSO [on (ArN₂)BF₄]

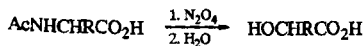
Helv 59 1427 (1976)



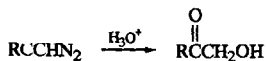
Tetr 32 1101 (1976)

JOC 56 2499 (1991); 59 3775 (1994)

SL 907 (1993)



TL 35 7731 (1994)



JACS 74 6221 (1952)

JCS B 1302 (1968)

TL 34 1733 (1993)

5. Acetate Substitution



BCSJ 55 3941 (1982)

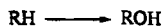
4. OXIDATION

1. Alkanes

Reviews:

Angew Int 17 909 (1978)

Russ Chem Rev 61 1033 (1992) (microbes)



Reagent(s)

RH



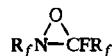
3° RH

JACS 108 2470 (1986); 116 2375 (1994)
JOC 57 2182, 5052 (1992); 58 5548 (1993)
TL 33 7411 (1992); 34 1131, 6103 (1993); 36
7999 (1995)



3° RH

JACS 111 6749 (1989); 115 7250 (1993)
(alkylammonium tetrafluoroborates); 116
2375 (1994)
TL 31 3067 (1990); 33 7411 (1992); 34 6103
(1993)
JOC 57 953 (1992)



3° RH

JACS 115 4897 (1993)
JOC 59 5511 (1994)

O₂, Me₂CHCH₂CHO, cat Fe[2-(
acetoacetoxy)ethyl methacrylate]₃

3° RH

TL 35 4193 (1994)

O₂, cat Co Schiff base, Me₂CHCHO

3° RH

TL 36 8497 (1995)

O₃, silica gel

3° RH

JOC 40 2141 (1975); 50 2759 (1985)
Org Syn Coll 6 43 (1988)

p-NO₂C₆H₄CO₃H

3° RH


Angew Int 18 407 (1979)

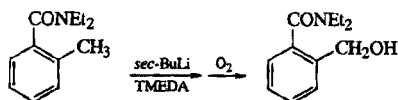
CF₃CO₃H

2° RH

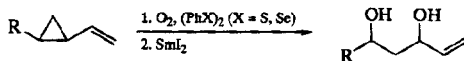
CC 1051 (1976)

RH \longrightarrow ROH (continued)

Reagent(s)	RH	
$\text{CH}_3\text{CO}_3\text{H}$, cat Ru-C	3° RH	TL 35 7953 (1994)
NaBr , NaOCl , $(n\text{-Bu}_4\text{N})\text{HSO}_4$	Ar_3CH	JOC 57 4555 (1992)
F_2 , H_2O , CH_3CN	3° RH	JACS 111 8325 (1989)
CrO_2Cl_2 , (ultrasound)/Zn	Ph_3CH	JOC 58 512 (1993)
$(\text{PhNEt}_3)\text{MnO}_4$	3° RH	Angew Int 18 68 (1979)
H_2O_2 , cat MeReO_3	3° RH	TL 36 6415 (1995)
NaIO_4 , cat RuCl_3	3° RH	JOC 57 5525 (1992)
RuO_4	3° RH	Acta Chem Scand B 40 430 (1986) TL 30 5271 (1989)
 , cat Ru porphyrin	3° RH	JACS 114 10660 (1992)
$\text{Et}_3\text{NO} \cdot 2\text{H}_2\text{O}$	ArCH_2R	TL 30 4857 (1989)
$(\text{NO}_2)\text{BF}_4$	3° RH	JOC 58 4639 (1993)
chloroperoxidase (enantioselective)	ArCH_2R	JACS 117 10419 (1995)
<i>Pseudomonas putida</i> (enantioselective)	ArCH_2R	TL 32 3887 (1991)
<i>Rhizopus nigricans</i>	2°, 3° RH	JOC 27 361 (1962) TL 32 5383 (1991)
<i>Rhizopus arrhizus</i>	2° RH	TL 33 7845 (1992)
<i>Bacillus cereus</i> (enantioselective)	1° RH	JOC 53 5700 (1988); 58 6329 (1993)
<i>Streptomyces griseus</i> (enantioselective)	2° RH	JOC 53 5700 (1988)
<i>Beauveria sulfurescens</i> (enantioselective)	1°, 2°, 3° RH	Tetr 43 2273 (1987) JOC 53 1797 (1988); 54 2478 (1989); 57 7209, 7212 (1992)



JOC 52 674 (1987)

TL 30 6985 (1989)
SL 217 (1995) (review)

2. Arenes



Reviews:

Adv Org Chem 1 103 (1960)

R. O. C. Norman, R. Taylor, "Electrophilic Substitution in Benzenoid Compounds," Elsevier, Amsterdam (1965)

"Applications of Biochemical Systems in Organic Chemistry," J. Wiley, New York (1976), Part I, pp 69-106

"Comprehensive Organic Chemistry," Pergamon, Oxford (1979), Vol 1

Russ Chem Rev 61 1130 (1992)

H_2O_2 , HF	<i>JOC</i> 35 4028 (1970); 56 6148 (1991)
H_2O_2 , HF, py	<i>Syn</i> 536 (1979) <i>JOC</i> 56 6148 (1991)
H_2O_2 , HF, BF_3	<i>JOC</i> 46 4305 (1981); 56 6148 (1991)
H_2O_2 , HF, SbF_5	<i>Nouv J Chim</i> 6 477 (1982) TL 27 4565 (1986) <i>JOC</i> 56 6148 (1991)
H_2O_2 , HF, TaF_5	<i>JOC</i> 56 6148 (1991)
H_2O_2 , FSO_3H	<i>JOC</i> 56 6148 (1991)
H_2O_2 , FSO_3H , SO_2	<i>JOC</i> 56 6148 (1991)
H_2O_2 , FSO_3H , SO_2ClF , (SbF_5)	<i>JOC</i> 43 865 (1977); 56 6148 (1991)
H_2O_2 , $\text{CF}_3\text{SO}_3\text{H}$, SO_2ClF	<i>JOC</i> 56 6148 (1991)
H_2O_2 , AlCl_3	<i>JOC</i> 36 3184 (1971)
H_2O_2 , FeSO_4 (on ArOH)	<i>J Prakt Chem</i> 152 46 (1939)
H_2O_2 or PhIO , cat Fe(III) or Mn(III) porphyrins	TL 31 6645 (1990)
<i>t</i> -BuO ₂ H, AlCl_3	BCSJ 43 293 (1970)
<i>t</i> -BuO ₂ H, KO- <i>t</i> -Bu, NH_3 (on ArNO_2)	<i>JOC</i> 55 4979 (1990)
$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, $\text{CF}_3\text{SO}_3\text{H}$	SL 39 (1991)
$(\text{Me}_3\text{SiO})_2$, $\text{CF}_3\text{SO}_3\text{H}$	<i>JOC</i> 54 1204 (1989)
$\text{CF}_3\text{CO}_2\text{H}$, CH_2Cl_2 , Et_3N , electrolysis	SL 661 (1995)
$\text{CF}_3\text{CO}_3\text{H}$	<i>JCS</i> 1804 (1959); 5404 (1964) <i>JOC</i> 27 627 (1962)
$\text{CF}_3\text{CO}_3\text{H}$, BF_3	<i>JACS</i> 85 2177 (1963) <i>JOC</i> 29 2397 (1964); 30 331 (1965)
$\begin{array}{c} \text{O} \quad \text{O} \\ \parallel \quad \parallel \\ i\text{-PrOCOOCO-}i\text{-Pr, AlCl}_3 \end{array}$	<i>JACS</i> 87 1566, 4811 (1965)
$\text{K}_2\text{S}_2\text{O}_8$, base (on ArOH or ArNR_2)	<i>JCS</i> 2303 (1948) <i>Chem Rev</i> 49 91 (1951) (review) <i>Org Rxs</i> 35 421 (1988) (review)

cyclopentadiene, $\text{H}_3\text{PO}_4/\text{PdCl}_2(\text{CH}_3\text{CN})_2/\text{H}_2\text{O}_2$,
HCl (on ArOH) TL 22 2327 (1981)

O_2 , $\text{HO}_2\text{CC}(\text{OH})=\text{C}(\text{OH})\text{CO}_2\text{H}$, peroxidase
catalyst (on ArOH) JACS 103 6263 (1981)



Reagents

X

n-BuLi / $\text{MoO}_5\cdot\text{py}\cdot\text{HMPA}$

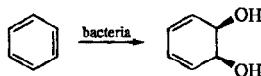
MeO

TL 28 2643 (1987)

sec-BuLi, TMEDA / O_2

MeO, CONEt_2

JOC 52 674 (1987)



Biochem 7 3795 (1968); 9 1626, 1631 (1970); 12 1520 (1973); 14 575 (1975)

Arch Biochem Biophys 142 394 (1971)

JACS 95 4048 (1973); 110 4735 (1988); 113 666 (1991); 116 1147 (1994)

Biochem Biophys Res Commun 50 211 (1973)

J Bacteriol 119 930 (1974); 166 1028 (1986); 168 55 (1986)

JCS Perkin I 2506 (1975)

Tetr 33 2491 (1977)

JOC 43 1023 (1978); 49 3621 (1984); 54 4239 (1989)

CC 954 (1983)

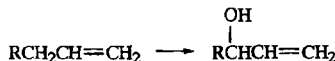
S. C. Taylor, "Enzymes in Organic Synthesis," Ciba Foundation Symposium 111, Pitman, London (1985),
p 71

TL 28 5173, 6391 (1987); 30 4053 (1989); 31 13 (1990) (naphthalene); 32 1671 (1991); 33 1241 (1992)

SL 309 (1990); 391 (1992)

3. Alkenes

See page 991, Section 1, for addition to the double bond; and page 231, Section 5, for oxidation with allylic transposition.



SeO_2

Org Rxn 5 331 (1949); 24 261 (1976)

JOC 35 1646, 1653 (1970); 44 4683 (1979); 51 256
(1986); 52 3468 (1987)

B. S. Thyagarajan, "Selective Organic Transformations," Vol 1 (1970), p 307

JACS 93 4835 (1971); 114 2560 (1992)

Syn 215 (1978)

CL 85 (1986)

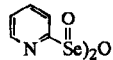
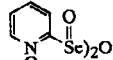
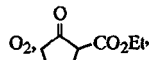
cat SeO_2 , H_2O_2

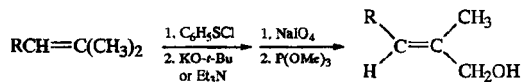
Org Syn Coll Vol 6 946 (1988)

JACS 112 462 (1990) (on enol silane)

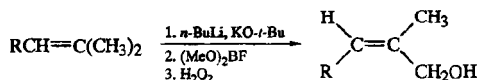
SeO_2 , *t*-BuO $_2\text{H}$

JACS 99 5526 (1977); 112 6942 (1990); 113 5765
(1991)

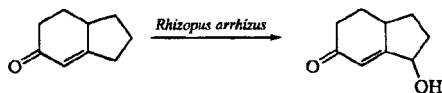
	JOC 48 1404 (1983); 50 1602 (1985); 52 3860 (1987); 57 4598 (1992)
	TL 27 2279 (1986); 28 1561, 5945 (1987)
SeO ₂ , <i>t</i> -BuO ₂ H, silica gel	CL 1703 (1981)
SeO ₂ , NMO	JOC 51 1635 (1986); 58 2523 (1993)
SeO ₂ , pyridine <i>N</i> -oxide	TL 32 6057 (1991)
	TL 35 5149 (1994)
	TL 35 5149 (1994)
O ₂ ,  cat Co Schiff's base	TL 35 4003 (1994)
O ₂ , Me ₂ CHCHO, cat Co(II) Schiff's base	TL 36 159 (1995)
RLi, TMEDA/O ₂	JACS 94 4298 (1972) Chem Pharm Bull 32 4632 (1984) JOC 51 4315 (1986)
<i>Mucor plumbeus</i>	TL 33 7845 (1992)
<i>Rhizopus arrhizus</i>	TL 32 647, 1983 (1991)
various fungal strains	TL 32 651 (1991)



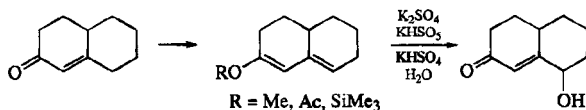
TL 4539, 5123 (1978)



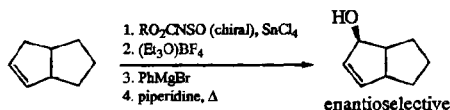
SL 173 (1994)



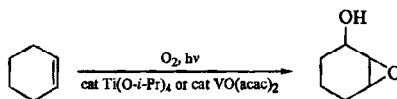
TL 32 3573 (1991)



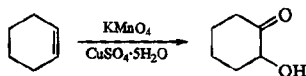
TL 22 4201 (1981)



JACS 109 2839 (1987); 112 7653 (1990)



JACS 111 203 (1989)



JOC 54 5182 (1989)



O_3/H_2 , Raney Ni

Can J Chem 38 1976 (1960)

$\text{O}_3/\text{BH}_3\text{-SMe}_2$

JOC 54 1430 (1989)

O_3/NaBH_4

JACS 74 3855 (1952); 98 1612 (1976)

JOC 19 1824 (1954); 25 108 (1960); 41 1396 (1976); 56 3102 (1991); 58 832 (1993); 59

2092 (1994); 60 3626, 5910 (1995)

Can J Chem 38 1976 (1960)

SL 114 (1992)

$\text{O}_3/\text{Me}_2\text{S}/\text{NaBH}_4$

JOC 56 5385 (1991)

$\text{O}_3/\text{LiAlH}_4$

Helv 33 1308 (1950)

JACS 74 3855 (1952); 79 3165 (1957); 90 1905, 1907 (1968)

JOC 20 803 (1955); 25 108 (1960); 54 3347 (1989)

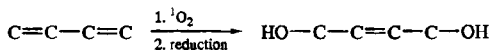
Angew 69 267 (1957)

Ber 111 3412 (1978)

$\text{Me}_3\text{SiO}_3\text{H}/\text{LiAlH}_4$

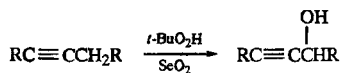
TL 32 4235 (1991)

4. Dienes



See page 1073, Section 1.

5. Alkynes



JOC 44 4202 (1979)

6. Alcohols

 H_2O_2 , HOAc, HClO_4

JOC 15 775 (1950)

 H_2O_2 , TsOH

JOC 51 5436 (1986); 52 5283 (1987); 59

5445 (1994)

SL 335 (1994)

 H_2O_2 , $\text{BF}_3 \cdot \text{OEt}_2$

JOC 51 5436 (1986)

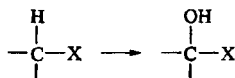
JACS 109 2717 (1987)

TL 28 1027 (1987)

 $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, $\text{BF}_3 \cdot \text{OEt}_2$

TL 34 7667 (1993)

7. Carbonyl Compounds



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 2.3, p 151

<u>X</u>	<u>Reagent(s)</u>	
CHO	LDA / $\text{MoO}_5 \cdot \text{py} \cdot \text{HMPA}$	JOC 53 855 (1988)
COR	PhIO , NaOH, MeOH	TL 22 1283 (1981)
		CC 641 (1981)
	$\text{PhI}(\text{OAc})_2$, NaOH, MeOH	TL 22 1283 (1981); 25 4745 (1984); 28
		5709 (1987)
		JACS 103 686 (1981)
	$\text{PhI}(\text{O}_2\text{CCF}_3)_2$, $\text{CF}_3\text{CO}_2\text{H}$, H_2O , CH_3CN	TL 33 6065 (1992)
	$o\text{-HO}_2\text{CC}_6\text{H}_4\text{IO}$, KOH, MeOH / H_3O^+	TL 25 691, 4745 (1984)
		Org Syn 64 138 (1985)
		Org Syn Coll Vol 7 263 (1990)
	$\text{Ti}(\text{NO}_3)_3$, HOAc	JOC 37 3381 (1972)
	NaOH, O_2 , $\text{P}(\text{OEt})_3$, chiral catalyst	TL 29 2835 (1988)
	NaH, $\text{P}(\text{OEt})_3 / \text{O}_2$	JOC 51 1478 (1986)
	NaO- <i>t</i> -Bu, O_2 , $\text{P}(\text{OEt})_3$	JOC 33 3294 (1968)
	KO- <i>t</i> -Bu, O_2 / Zn, HOAc	JCS 1578 (1962)
		JACS 90 2448 (1968)

X

Reagent(s)

LiN(SiMe₃)₂/O₂, P(OEt)₃

JOC 51 3393 (1986); 54 4576 (1989)

NaN(SiMe₃)₂/ $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$

JOC 59 2358 (1994)

LDA/ $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$

TL 32 715 (1991)

Ber 124 2369 (1991)

LDA/Cp₂TiCl₂/ $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$

JOC 59 2358 (1994)

LDA/(Et₂N)₃TiCl/ $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$

JOC 59 2358 (1994)

LDA/(i-PrO)₃TiCl/ $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C}=\text{O} \\ \diagdown \\ \text{CH}_3 \end{array}$

JOC 59 2358 (1994)

(PhSeO)₂O

CL 763 (1979)

Tetr 37 473 (1981)

base/MoO₅·py·HMPA

JACS 96 5944 (1974); 106 3539, 4547 (1984); 112 5276 (1990); 115 3146 (1993)

JOC 43 188 (1978); 53 4855 (1988); 54 3334, 3354 (1989)

Org Syn 64 127 (1985)

Org Syn Coll Vol 7 277 (1990)

SL 337 (1994)

LDA/MoO₅·py·MeN $\begin{array}{c} \text{O} \\ \parallel \\ \text{N} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \end{array}$ ·NMe

SL 107 (1990)

base/PhSO₂N $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \end{array}$ ·CHPh

JOC 49 3241 (1984); 52 4592 (1987); 53 4314 (1988); 57 3274, 4043 (1992); 58 4963, 7728 (1993); 60 889, 1413, 4549 (1995)

TL 30 1579 (1989); 31 3615 (1990)

base / chiral RSO₂N $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH}_2 \quad \text{CH}_2 \end{array}$ ·CR₂

JOC 51 4083 (1986); 53 4314 (1988); 54 2021 (1989); 55 3715 (1990); 56 809, 1143 (1991); 57 7274 (1992); 58 1751 (1993); 59 1184 (1994); 60 4549 (1995)

TL 30 779, 1613 (1989); 31 6823 (1990); 32 7671 (1991)

JACS 112 6679 (1990); 113 4037 (1991); 114 9419 (1992)

Chem Rev 92 919 (1992) (review)

CO₂HLDA/O₂

JOC 40 3253 (1975)

Syn Commun 9 63 (1979)

TL 27 2199 (1986)

CO₂RLDA/O₂

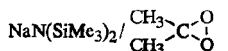
TL 1731 (1975)

JACS 112 8100 (1990)

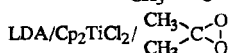
JOC 52 3323 (1987)

KN(SiMe₃)₂/(EtO)₃P, O₂

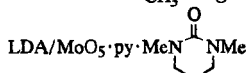
JOC 53 4724 (1988)



JOC 59 2358 (1994)



JOC 59 2358 (1994)



SL 107 (1990)

TL 31 3437 (1990)

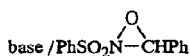
JACS 96 5944 (1974)

base / $\text{MoO}_5 \cdot \text{py} \cdot \text{HMPA}$

JOC 43 188 (1978); 46 4825 (1981); 52 1170, 3346 (1987); 53 4724 (1988) (lactone)

TL 26 203 (chiral), 5631 (1985); 27 1833, 3999 (1986); 28 221, 1147, 6381 (lactone) (1987); 30 1029 (1989) (lactone); 33 4637 (1992); 34 2787 (1993)

Helv 69 615 (1986)



JOC 49 3241 (1984); 53 4724 (1988);

58 1003 (1993); 60 2683 (1995)

JACS 110 649 (1988)

TL 30 1029 (1989) (lactone); 34 7557 (1993) (lactone)



JOC 51 2402 (1986); 52 5288 (1987);

55 3715 (1990); 56 809 (1991); 57

3337 (1992); 59 1184 (1994); 60

6148 (1995)

TL 30 1613 (1989); 34 3715 (1993)

Chem Rev 92 919 (1992) (review)

CONR₂LDA / O₂LDA / P(OEt)₃ / O₂LDA / MoO₅ · py · HMPA

TL 1731 (1975)

JOC 52 4352 (1987)

JOC 50 2170 (1985)

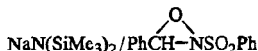
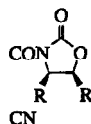
TL 34 6325 (1993)



JOC 51 2402 (1986); 52 5288 (1987)

Chem Rev 92 919 (1992) (review)

TL 36 4397 (1995)

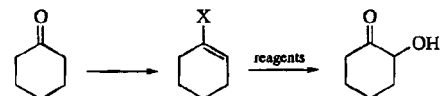


JACS 107 4346 (1985) (chiral); 114 9434 (1992) (chiral)

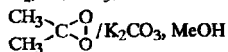
LDA / O₂ / SnCl₂LDA / MoO₅ · py · HMPA

JOC 40 269 (1975)

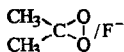
JOC 41 740 (1976)

XOSiMe₃Reagent(s)O₂, hv / PPh₃ / MeOH

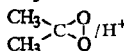
TL 2375 (1977)



JACS 115 354 (1993)

XReagent(s)OSiMe₃ (continued)

JOC 59 2358 (1994); 60 889 (1995)



JOC 60 3385 (1995)

TL 36 675 (1995)

t-BuO₂H, cat VO(acac)₂

JOC 58 4189 (1993)

CH₃CO₃H

JACS 110 6558 (1988)

m-ClC₆H₄CO₃H/H₃O⁺ or F⁻

TL 4319 (1974); 2935 (1976); 4603 (1978); 28 435, 581, 3723, 5017 (1987); 30 3323 (1989)

JOMC 77 C19 (1974)

JOC 40 3427 (1975) (alkanal also);

42 1581 (1977); 43 1599 (1978);

52 3745 (1987); 54 4083 (1989);

55 2694, 2829 (1990); 60 1413

(1995)

CC 27 (1977)

Org Syn 64 118 (1985)

JACS 109 7575 (1987); 110 6558

(1988); 115 3146 (1993); 117 1908

(1995)

Org Syn Coll Vol 7 282 (1990)

TL 22 607 (1981)

JOC 54 3334 (1989); 58 4662 (1993)

TL 30 7463 (1989)

cat OsO₄, NMO/H₃O⁺

JACS 115 8463 (1993)

cat OsO₄, NMO, quinuclidine/
Na₂S₂O₅cat OsO₄, K₃Fe(CN)₆, cat 2,5-di-
phenyl-4,6-bis(9-*O*-dihydroquinidyl
or quinine)pyrimidine, K₂CO₃,
MeSO₂NH₂ (chiral)

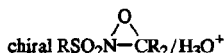
JACS 115 8463 (1993)

cat OsO₄, K₃Fe(CN)₆, cat 1,4-
bis(9-*O*-dihydroquinidyl or
quinine)phthalazine, K₂CO₃,
MeSO₂NH₂ (chiral)cat OsO₄, K₃Fe(CN)₆, cat 9-*O*-
phenanthryl-dihydroquinine or
-dihydroquinidine, K₂CO₃ (chiral)

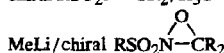
TL 35 7813 (1994)

CrO₂Cl₂

TL 23 2917 (1982)



JOC 52 954 (1987)



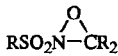
TL 29 4269 (1988)

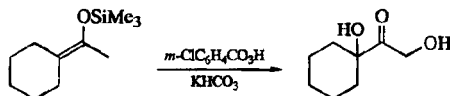
p-NO₂C₆H₄SO₃)₂/K₂CO₃/HCl
PhIO, BF₃·OEt₂, H₂O

JOC 50 5148 (1985); 51 130 (1986)

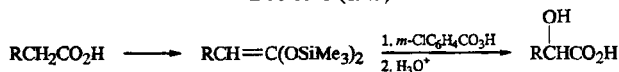
JCS Perkin I 1781 (1987)

JOC 54 4008 (1989)

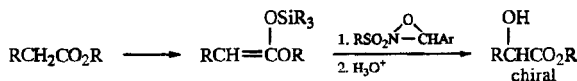
OSiR ₂ OR	<i>m</i> -ClC ₆ H ₄ CO ₃ H / <i>n</i> -Bu ₄ NF	JOC 53 921 (1988)
OAc	(<i>p</i> -NO ₂ C ₆ H ₄ SO ₃) ₂ / K ₂ CO ₃ / HCl	Syn 760 (1985) JOC 51 130 (1986) TL 34 4431 (1993) JOC 60 4822 (1995)
	<i>m</i> -ClC ₆ H ₄ CO ₃ H / KOH	
	<i>m</i> -ClC ₆ H ₄ CO ₃ H, NaHCO ₃ / KOH	
OR	—	See page 991, Section 5.
NR ₂	O ₃	TL 21 523 (1980)
	(PhCO ₂) ₂	JOC 28 581 (1963)
	(<i>p</i> -NO ₂ C ₆ H ₄ SO ₃) ₂ / K ₂ CO ₃ / HCl	JOC 50 5148 (1985); 51 130 (1986)
		TL 29 4365 (1988)



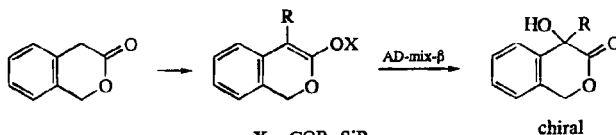
TL 30 3323 (1989)



JOC 40 3253 (1975)





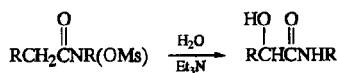
JOC 52 954 (1987)

X = COR, SiR₃

JOC 59 6139 (1994)



X	Reagent(s)	
R	 , (<i>n</i> -Bu ₄ NF or KF)	Ber 124 2369 (1991)
OR	O ₂ , rose bengal, <i>n</i> -Bu ₄ NF, hv	IACS 104 4695 (1982)
	 , (<i>n</i> -Bu ₄ NF or KF)	Ber 124 2369 (1991)
	base / <i>N</i> -sulfonylaziridine	TL 32 867 (1991) (chiral) JOC 59 1184 (1994) (chiral)
NR ₂	KO- <i>t</i> -Am, O ₂ , P(OMe) ₃	JOC 55 5572 (1990)

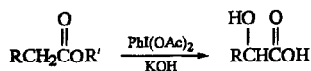


JOC 57 5700 (1992)

JACS 114 6262 (1992)



See page 231, Section 5.



TL 22 2747 (1981)



Review: Org Rxs 43 251 (1993)

 H_2O_2 , NaOH

TL 28 455 (1987)

 $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$, ultrasound

TL 33 865 (1992)

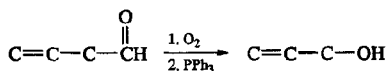
 PhCO_3H

JOC 34 3985 (1969)

 $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$

JCS Perkin I 1353 (1974)

JOC 60 6592 (1995)



BCSJ 64 3735 (1991)

JACS 115 3056 (1993)

 $h\nu$, O_2 , acridine/ Me_2S

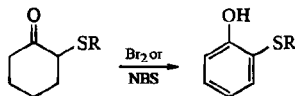
TL 33 83 (1992)

 $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$, DCC/(ArS) $_2$, Na_2HPO_4

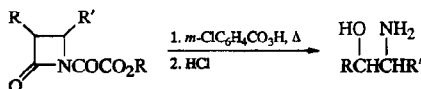
TL 28 4489 (1987)

 PhIO , cat Fe porphyrin

TL 33 4949 (1992)



TL 35 7413 (1994)

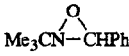
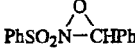
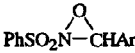
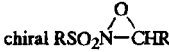



J Antibiotics 33 796 (1980)

8. Organometallics



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Parts 4.1 (B) and 4.3 (Si)

<u>M</u>	<u>Reagent(s)</u>	
Li	—	See page 975, Section 1.
	MoO ₅ ·py·HMPA	JOC 50 5660 (1985) (CH ₂ -oxazoline)
	(Me ₃ SiO) ₂ /HCl	Syn 633 (1986) (1°, 2° alkyl; aryl)
	LiO ₂ - <i>t</i> -Bu	SL 233 (1993) (aryl)
	 Me ₃ CN—CHPh	JACS 101 1044 (1979) (aryl)
MgX	 PhSO ₂ N—CHPh	JACS 101 1044 (1979) (1° alkyl, aryl)
	—	JOC 50 5660 (1985) (CH ₂ -oxazoline)
	—	TL 28 5115 (1987) (aryl)
	MoO ₅ ·py·HMPA	JOC 42 1479 (1977) (aryl)
	 PhSO ₂ N—CHAr	JACS 101 1044 (1979) (1° alkyl, aryl)
B	—	TL 28 5115 (1987)
	oxone®	(1°, 2° alkyl; aryl)
	H ₂ O ₂ , KF, KHCO ₃	TL 28 5115 (1987) (aryl)
	 chiral RSO ₂ N—CHR	TL 28 5115 (1987) (aryl)
	—	See page 1005, Section 6.
B(OH) ₂ , B(OR') ₂	—	TL 36 5117 (1995) (aryl)
SiHMe ₂	H ₂ O ₂ , KF, KHCO ₃	SL 1243 (1995) (2° alkyl)
SiMc ₃	<i>m</i> -ClC ₆ H ₄ CO ₂ H/ <i>n</i> -Bu ₄ NF·3H ₂ O	TL 30 6067 (1989) (allylic rearrangement)
	Hg(OAc) ₂ /BH ₃ /H ₂ O ₂ , NaOH	JCS Perkin I 2463 (1989)
	—	SL 521 (1990) (both aryl)
	—	TL 28 4229 (1987) (2° alkyl); 29 2077 (1988) (2° alkyl); 30 229 (1989) (1° alkyl); 31 5997 (1990) (2° alkyl)
SiMe ₂ Ph	KBr, CH ₃ CO ₂ H, NaOAc, HOAc	TL 28 4229 (1987); 31 3645 (1990) (both 2° alkyl)
	Hg(OAc) ₂ , CH ₃ CO ₂ H, HOAc	TL 28 4229 (1987) (2° alkyl)
	cat Hg(OAc) ₂ , cat Pd(OAc) ₂ , CH ₃ CO ₂ H, HOAc	TL 26 397 (1985) (2° alkyl)
	<i>m</i> -ClC ₆ H ₄ CO ₂ H, KF	CC 29 (1984) (1°, 2° alkyl); 318 (1985) (2° alkyl)
	HBf ₄ / <i>m</i> -ClC ₆ H ₄ CO ₂ H, Et ₃ N	Helv 69 1542 (1986) (2° alkyl)

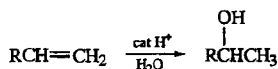
M	Reagent(s)	
	BF ₃ ·2HOAc / <i>m</i> -ClC ₆ H ₄ CO ₃ H, Et ₃ N	CC 305 (1986) (2° alkyl)
	BF ₃ ·2HOAc / CH ₃ CO ₃ H, Et ₃ N	CC 1198 (1986) (2° alkyl)
	BF ₃ ·2HOAc / <i>m</i> -ClC ₆ H ₄ CO ₃ H, KF	CC 29 (1984) (2°, 3° alkyl)
	H ₂ O ₂ , KOH	TL 33 5807 (1992) (2° alkyl)
	Li, NH ₃ , EtOH / <i>n</i> -Bu ₄ NF / H ₂ O ₂ , KHCO ₃ , MeOH	TL 36 351 (1995) JOC 60 5537 (1995) (both 2° alkyl)
SiMe ₂ Ar	CF ₃ CO ₂ H / H ₂ O ₂ , KF, KHCO ₃ , MeOH	TL 36 501 (1995) (2° allylic)
SiMe ₂ CH ₂ N 	H ₂ O ₂ , KF	JOC 57 6107 (1992) (2° benzylic)
SiMe ₂ CH ₂ NR ₂	H ₂ O ₂ , KF, KHCO ₃	TL 34 1449 (1993) (2° propargylic)
SiPh ₂ CH ₂ CMe=CHMe	BF ₃ ·2HOAc or HCl / H ₂ O ₂ , KF, KHCO ₃	TL 34 7287 (1993) (1°, 2° allylic; 2° benzylic)
	BF ₃ ·2HOAc / H ₂ O ₂ , KF, NaHCO ₃	TL 36 1733 (1995) (2° allylic)
	CH ₃ CO ₃ H, KBr, NaOAc, HOAc	TL 34 7287 (1993) (2° benzylic)
	H ₂ O ₂ , KF, KBr, NaHCO ₃	TL 34 7287 (1993) (1°, 2° allylic)
SiPh ₂ Me	BF ₃ ·2HOAc / H ₂ O ₂ , HF, NaHCO ₃	SL 378 (1995) (2° alkyl)
SiPh ₃	<i>n</i> -Bu ₄ NF / H ₂ O ₂ , KF, NaHCO ₃	SL 378 (1995) (2° alkyl)
SiMe ₂ SiMe ₂ R (R = Me, Ph)	<i>n</i> -Bu ₄ NF / H ₂ O ₂ , KHCO ₃	SL 941 (1995) (1° alkyl, aryl)
SiMe(OEt) ₂	air, hydroquinone, <i>n</i> -Bu ₄ NF	TL 30 6533 (1989) (1°, 2° alkyl)
	H ₂ O ₂ , HCO ₃ ⁻ or CO ₃ ²⁻	Organomet 2 1694 (1983) (1° alkyl)
	H ₂ O ₂ , KF or KHF ₂	Organomet 2 1694 (1983) (1° alkyl)
	<i>t</i> -BuO ₂ H, KHF ₂	Organomet 2 1694 (1983) (1° alkyl)
	<i>m</i> -ClC ₆ H ₄ CO ₃ H	Organomet 2 1694 (1983) (1° alkyl)
SiMe ₂ OH	H ₂ O ₂ , KF	Angew Int 33 99 (1994) (3° alkyl)
SiMe ₂ OR	H ₂ O ₂ , NaHCO ₃	TL 25 4245 (1984) (1° alkyl); 27 3377 (1986) (2° alkyl)
	H ₂ O ₂ , KHCO ₃	TL 33 465 (1992) (1° allylic)
	H ₂ O ₂ , KHCO ₃ , KF	TL 31 7563 (1990); (2° allylic); 34 2927 (1993) (2° alkyl)
	H ₂ O ₂ , Na ₂ CO ₃	JOC 54 1157 (1989) (1° alkyl)
	H ₂ O ₂ , K ₂ CO ₃ , KF	TL 35 1657 (1994) (1° alkyl)

	H ₂ O ₂ , KOH	TL 33 5807 (1992) (2° alkyl)
SiR'(Ph)OEt	<i>m</i> -ClC ₆ H ₄ CO ₃ H, KF	Tetr 39 983 (1983) (1° alkyl)
SiR' ₂ OEt	<i>m</i> -ClC ₆ H ₃ CO ₃ H, KF	Tetr 39 983 (1983) (aryl)
SiPh ₂ OEt	H ₂ O ₂ , KF, KHCO ₃	JACS 114 3989 (1992) (2° alkyl, 1° allylic)
SiPh ₂ OAc	H ₂ O ₂ , KHF ₂ , KHCO ₃	JOC 56 7076 (1991) (2° benzylic)
SiMe ₂ F	H ₂ O ₂ , KF, KHCO ₃	TL 32 7513 (1991) (3° cyclopropyl, 1° benzylic)
	H ₂ O ₂ , NaHCO ₃	TL 25 4249 (1984) (1° alkyl)
SiR _n F _{3-n} (n = 1, 2)	<i>m</i> -ClC ₆ H ₄ CO ₃ H, KF	Tetr 39 983 (1983) (1° alkyl)
SiF ₃	Me ₃ NO	TL 30 4375 (1989) (1°, 2° alkyl; allylic; aryl)
	<i>m</i> -ClC ₆ H ₄ CO ₃ H	Tetr 39 983 (1983) (1°, 2° alkyl; aryl)
SiF ₅ ²⁻	<i>m</i> -ClC ₆ H ₄ CO ₃ H	JACS 100 2268 (1978) Tetr 39 983 (1983) (both 1°, 2° alkyl; aryl)
SnR' ₃ (R' = Me, <i>n</i> -Bu)	Br ₂ / <i>m</i> -ClC ₆ H ₄ CO ₃ H, NH ₃	TL 30 6461 (1989) (2° alkyl)
ZnX	air	TL 36 3157 (1°, 2° alkyl), 3161 (1° alkyl) (1995)

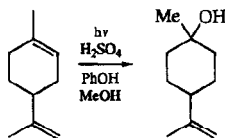
5. ALKENE, DIENE AND ALKYNE ADDITIONS

See also page 1005, Section 6.

1. Alkenes



JACS 40 822, 1950 (1918); 46 1512 (1924); 49 873 (1927); 56 460, 2138 (1934); 61 940 (1939); 73 3792 (1951); 74 5372 (1952); 77 1584 (1955); 79 3724 (1957); 93 4907 (1971)
JCS 4203 (1960)



Org Syn Coll Vol 7 304 (1990)



O₂, cat Co(acac)₂, *i*-PrOH

CL 449 (1989)

O₂, cat Co(CF₃COCHCOCH₃)₂, *i*-PrOH

CL 515 (1989)

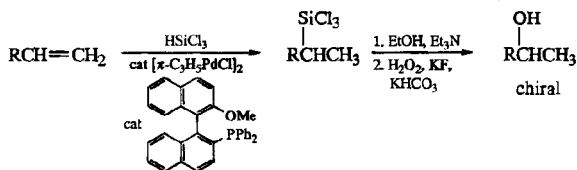
O₂, cat Co(CF₃COCHCOCH₃)₂, Et₃SiH, *i*-PrOH

CL 569 (1989)

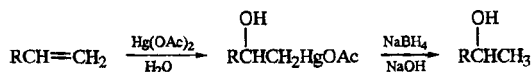
O₂, cat Co(acac)₂, PhSiH₃

CL 1071 (1989)

JOC 60 4339 (1995)



JACS 113 9887 (1991)



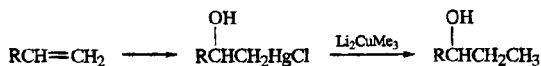
Review: R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 2

JACS 89 1522, 1524, 1525 (1967); 102 7798 (1980) (diene regioselectivity)

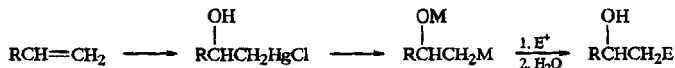
JOC 35 1844 (1970); 39 1474 (1974); 44 1910 (1979); 46 531, 930, 3810 (1981); 54 4479 (1989)

Org Syn Coll Vol 6 766 (1988)

TL 33 4863 (1992) [$\text{Hg}(\text{BF}_4)_2$, diene regioselectivity]



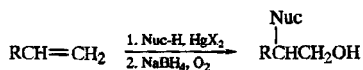
Organomet 1 74 (1982)



M = alkali metal; $\text{E}^+ = \text{D}_2\text{O}, \text{O}_2, \text{CO}_2, \text{RCHO}, \text{R}_2\text{CO}, \text{Me}_3\text{SiCl}, (\text{MeS})_2, \text{R}_2\text{C}=\text{NR}$

TL 2015 (1978)

JOC 44 4798 (1979); 47 1560 (1982)



Nuc-H

C=C

JACS 102 1742 (1980) (intramolecular)

TL 25 2945, 5071 (1984) (both intramolecular)

ROH

JACS 96 870 (1974); 108 2758 (1986)

(intramolecular)

JOC 47 4919 (1982) (intramolecular)

ROOH

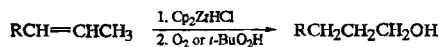
TL 25 5013 (1984) (intramolecular)

R_2NH

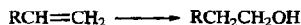
TL 26 1123 (1985) (intramolecular)

RO_2CNHR

TL 29 1627 (1988) (intramolecular)



TL 3041 (1975); 23 157 (1982)

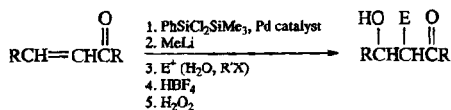


$\text{H}_2\text{O}, h\nu$

JOC 54 1354 (1989)

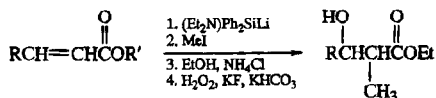
$(\text{PhCH}_2\text{NEt}_3)\text{BH}_4, \text{Me}_3\text{SiCl}/\text{K}_2\text{CO}_3$

CC 903 (1989)

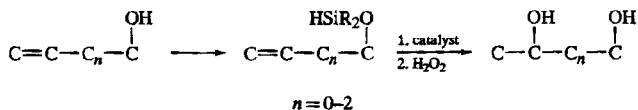


TL 29 4147 (1988)

JACS 110 5579 (1988)



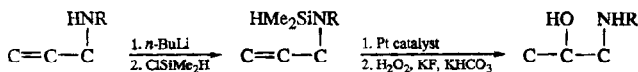
JACS 114 3989 (1992)



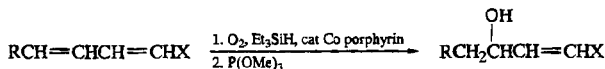
Catalyst

Pt JACS 108 6090 (1986); 110 3712 (1988); 115 10400 (1993)
TL 27 3377 (1986)

Rh JACS 110 3712 (1988); 114 2121, 2128 (1992) (both chiral)
TL 31 7333 (1990) (chiral)

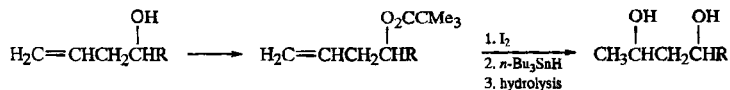


JOC 55 3438 (1990)

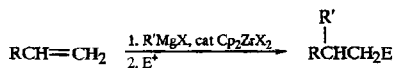


X = CHO, COR, CO₂R, CONHR, CN

TL 36 1879 (1995)



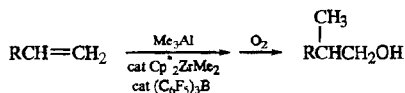
JACS 106 5304 (1984)


$$E^+ = RCHO, R_2CO, B(OMe)_3 / H_2O_2 \text{ (E=OH)}, O_2 \text{ (E=OH)}$$

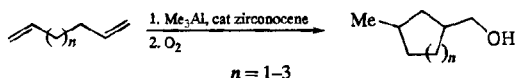
JACS 113 5079, 8950 (1991); 115 6614 (1993); 117 10771 (1995) (chiral zirconocene)

TL 32 6797 (1991)

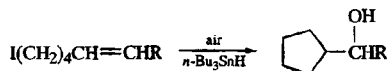
JOC 58 4237 (1993) (chiral zirconocene)



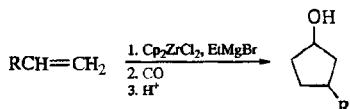
JACS 117 5873 (1995)



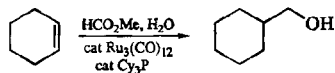
JACS 117 5873, 10771 (chiral) (1995)



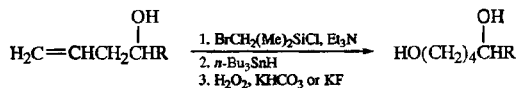
JACS 113 8980 (1991)



JACS 113 6266 (1991)



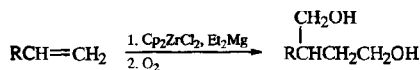
TL 32 505 (1991)



TL 29 4001 (1988)

JACS 112 8175 (1990)

JOC 55 3484 (1990); 56 3973 (1991)



JACS 113 6268 (1991)



Reviews:

Adv Org Chem 1 103 (1960)

Chem Rev 80 187 (1980) (OsO₄); 94 2483 (1994) (asymmetric)

Tetr Asym 3 1317 (1992) (asymmetric)

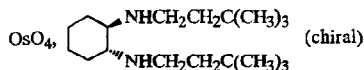
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 3.3, p 437

"Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 4

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21e, G. Thieme, Stuttgart-New York (1995), p 4547

cis hydroxylation

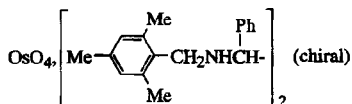
KMnO ₄	Org Syn Coll Vol 2 307 (1943) JACS 78 5342 (1956) JOC 53 929 (1988); 54 2730 (1989)
KMnO ₄ , 18-crown-6	JOC 53 929 (1988)
KMnO ₄ , dicyclohexano-18-crown-6	JOC 56 2135 (1991)
KMnO ₄ , (PhCH ₂ NEt ₃)Cl	TL 21 177 (1980) JOC 54 2730 (1989)
KMnO ₄ , NaOH, (PhCH ₂ NEt ₃)Cl	TL 4907 (1972) JOC 54 2730 (1989)
(<i>n</i> -C ₁₆ H ₃₃ NMe ₃)MnO ₄	Syn 431 (1984) JOC 54 2730 (1989)
(Ph ₃ PMe)MnO ₄	Tetr 35 1109 (1979)
OsO ₄	JOC 25 257 (1960) TL 35 2495 (1994)
OsO ₄ , py	Tetr 40 2247 (1984) (on allylic alcohols) JOC 52 2301 (1987) TL 28 4955 (1987); 31 6437 (1990); 32 635 (1991); 34 8275 (1993)
OsO ₄ , dihydroquinidine acetate (chiral)	JACS 102 4263 (1980) TL 28 3139 (1987)
OsO ₄ , dihydroquinidine <i>p</i> -chlorobenzoate (chiral)	TL 34 8275 (1993)
OsO ₄ , cat dihydroquinidine <i>p</i> -chlorobenzoate (chiral)	JACS 110 1968 (1988)
OsO ₄ , dihydroquinine acetate (chiral)	JACS 102 4263 (1980) TL 28 3139 (1987)
OsO ₄ , dihydroquinine <i>p</i> -chlorobenzoate (chiral)	TL 34 8275 (1993)
OsO ₄ , quinuclidine (chiral)	TL 28 3139 (1987)
OsO ₄ , (-)-(R,R)- <i>N,N,N',N'</i> -tetramethylcyclohexane-1,2- <i>trans</i> -diamine (chiral)	TL 27 3951 (1986)



JOC 58 1991 (1993)

OsO₄, chiral diamines derived from tartaric acid (chiral)

CL 131 (1986)

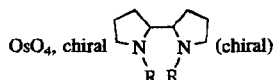


JACS 111 9243 (1989)

TL 31 2665 (1990); 36 2427, 2431 (1995)

OsO₄, chiral bis(piperazine) (chiral)

TL 33 4021 (1992)

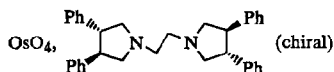


CC 665 (1989)

JOC 54 5834 (1989)

SL 705 (1992)

TL 34 3573 (1993)



JACS 109 6213 (1987)

TL 29 573 (1988); 31 1741 (1990)

cat OsO₄, H₂O₂

JACS 70 1484 (1948)

cat OsO₄, *t*-BuO₂H

JOC 59 1375 (1994)

cat OsO₄, *t*-BuO₂H, (Et₄N)OH

JACS 98 1986 (1976)

cat OsO₄, *t*-BuO₂H, (Et₄N)OAc

JOC 43 2063 (1978); 59 1375 (1994)

cat OsO₄, *t*-BuO₂H, (Et₄N)OAc, cat dihydroquinidine *p*-chlorobenzoate or cat bis dihydroquinidine terephthalate (chiral)

JOC 59 1375 (1994)

cat OsO₄, Me₃NO·2H₂O

JACS 109 3402 (1987); 112 4873 (1990); 114 980 (1992)

JOC 53 929 (1988); 54 2742 (1989); 57 6097 (1992);

58 294 (1993); 59 3055 (1994); 60 4932 (1995)

TL 30 7385 (1989); 36 1319 (1995)

cat OsO₄, Me₃NO·2H₂O, py

TL 21 449 (1980)

JACS 109 3353 (1987)

JOC 54 2742 (1989)

cat OsO₄, NMO·2H₂O

TL 1973 (1976); 28 1603, 5473 (6-hydroxy-2,4-alkadienoate ester to 5,6-dihydroxy-2-alken-4-olide), 5755 (1987); 31 161 (1990); 32 1003 (1,3-dienes and 1,3,5-triene to polyols), 2659 (1991); 33 3363, 6379 (1992)

Tetr 40 2247 (1984) (on allylic alcohols)

JACS 107 2712, 3891 (1985); 108 1094 (1986); 109 5437 (1987); 111 6861 (1989)

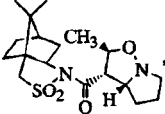
JOC 51 2637 (1986); 52 3745, 3784, 4505, 5624, 5700 (1987); 55 1698, 5424 (1990); 57 3078 (1992); 60 1848 (1995)

Org Syn Coll Vol 6 342 (1988)

SL 672 (1993)

- cat OsO₄, NMO, cat dihydroquinidine
p-chlorobenzoate (chiral) JACS 110 1968 (1988); 111 737, 1123 (1989)
TL 30 2041 (1989); 31 161 (1990); 36 2685 (1995)
JOC 55 1957 (1990); 59 7395 (1994)
SL 423 (1994)
- cat OsO₄, NMO, cat dihydroquinine
p-chlorobenzoate (chiral) JACS 110 1968 (1988); 111 737, 1123 (1989); 114
2524 (1992); 115 12226 (1993)
TL 31 161 (1990)
- cat OsO₄, NMO, cat dihydroquinine or
dihydroquinidine on polymer (chiral) TL 33 5453 (1992)
- cat OsO₄, NMO, cat 9-*O*-acylquinine-polymer
(chiral) TL 32 5175 (1991)
- cat OsO₄, NMO, cat 9-*O*-aryldihydroquinidine
(chiral) TL 31 3817 (1990); 33 7057 (1992)
- cat OsO₄ or K₂OsO₂(OH)₄, K₃Fe(CN)₆, cat
9-*O*-aryldihydroquinidine, K₂CO₃ (chiral) TL 31 4317 (1990); 32 5761 (1991); 33 2095, 3833,
6407 (1992); 34 2509 (1993)
JOC 56 4585 (1991); 58 844 (1993)
- cat OsO₄ or K₂OsO₂(OH)₄, K₃Fe(CN)₆, cat
9-*O*-aryldihydroquinine, K₂CO₃ (chiral) JOC 56 4585 (1991); 58 844 (1993)
TL 32 5761 (1991); 34 2509 (1993); 36 6519 (1995)
- cat OsO₄, K₃Fe(CN)₆, K₂CO₃ JOC 55 766 (1990)
TL 33 3363 (1992)
- cat OsO₄, K₃Fe(CN)₆, cat chiral diamine,
K₂CO₃ (chiral) TL 33 639 (1992)
- cat OsO₄, K₃Fe(CN)₆, K₂CO₃, MeSO₂NH₂ JACS 115 7047 (1993)
TL 35 2495 (1994)
- cat OsO₄, K₃Fe(CN)₆, cat quinuclidine, K₂CO₃,
MeSO₂NH₂ (chiral) JACS 115 7047, 7864 (1993)
TL 34 5575 (1993); 35 2495 (1994)
- cat OsO₄, K₃Fe(CN)₆, cat (9-*O*-indolinylcar-
bamoyl)dihydroquinidine, K₂CO₃ (chiral) JACS 114 7568 (1992)
TL 35 843, 4685, 6755 (1994)
JOC 59 6895 (1994)
- cat OsO₄, K₃Fe(CN)₆, cat di(dihydroquinidine)
terephthalate, K₂CO₃ (chiral) TL 34 3911 (1993)
- cat OsO₄ or K₂OsO₂(OH)₄, K₃Fe(CN)₆, cat
1,4-bis-(9-*O*-dihydroquinidine)phthalazine,
K₂CO₃, MeSO₂NH₂ (chiral, AD-mix-β) JACS 114 7570 (1992) (1,3-, 1,4- and 1,5-dienes to
enediols); 115 4891, 7047, 7864, 8463, 12226
(1993); 116 558 (1994)
TL 33 3833 (enzymes), 4273, 6407, 6411 (1992); 34
1893, 2079, 2083, 4675, 5031, 5545, 5575, 6485,
6925, 8225 (1993); 35 53, 425, 543, 843, 2495,
3469, 4389, 4685, 5129, 5611, 6275, 7315, 9445
(1994); 36 1055, 1359, 1981, 2199, 2685, 5969,
7549 (1995)
JOC 57 2768 (1992); 58 844, 7789 (1993); 59 54,
949, 2570, 3442, 5488, 5799, 6136, 6139, 6895
(1994); 60 5048 (1995)
Tetr 48 10515 (1992)
SL 603, 605 (1993); 119 (1994); 257, 903, 1029
(1995)
Tetr Asym 5 1473 (1995)

- AD-mix- β , $K_2S_2O_8$ JOC 59 2630 (1994)
- cat OsO_4 , $K_3Fe(CN)_6$, cat various modified quinidinephthalazine ligands, K_2CO_3 (chiral) TL 34 7375 (1993)
- cat $K_2OsO_4 \cdot 2H_2O$, $K_3Fe(CN)_6$, cat 1,4-bis-[*O*-6'-(4-heptyl)hydrocupreidy]naphthopyridazine, K_2CO_3 , $CH_3SO_2NH_2$ (chiral) TL 36 8741 (1995)
- cat OsO_4 , $K_3Fe(CN)_6$, various chiral ligands, K_2CO_3 , $MeSO_2NH_2$ (chiral) TL 34 5575 (1993)
- cat OsO_4 or $K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, cat 1,4-bis(9-*O*-dihydroquinine)phthalazine, K_2CO_3 , $MeSO_2NH_2$ (chiral, AD-mix- α) TL 33 6407, 6411, 6563 (1992); 34 1893, 5575, 6485, 6925, 8369 (1993); 35 53, 425, 543, 843, 5611, 6275, 9445 (1994); 36 2199, 2685, 4171, 4193, 5967 (1995)
JOC 57 2768 (1992); 58 844, 6151, 7789 (1993); 59 54, 949, 3442, 6139 (1994)
Tetr 48 10515 (1992)
JACS 115 7864, 8463, 12226 (1993); 117 193, 10805 (1995)
SL 47 (1993); 119, 263 (1994)
- AD-mix- α , $K_2S_2O_8$ JOC 59 2630 (1994)
- cat $K_2OsO_2(OH)_4$, NMO, cat 1,4-bis(9-*O*-dihydroquinine)phthalazine (chiral) JOC 59 5104 (1994)
- cat $K_2OsO_2(OH)_4$, NMO, cat 1,4-bis(9-*O*-dihydroquinidine)phthalazine (chiral) JOC 59 8302 (1994)
- cat $K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, cat 6,7-diphenyl-1,4-bis(9-*O*-dihydroquinidine)-phthalazine, K_2CO_3 , $MeSO_2NH_2$ (?) (chiral) JOC 60 3940 (1995)
- cat $K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, cat 6,7-diphenyl-1,4-bis(9-*O*-dihydroquinine)-phthalazine, K_2CO_3 , $MeSO_2NH_2$ (?) (chiral) JOC 60 3940 (1995)
- cat $K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, cat 2,3-diphenyl-5,8-bis(9-*O*-dihydroquinidine)-pyrazino[2,3-*d*]pyridazine, K_2CO_3 (chiral) TL 34 7375 (1993)
Tetr Asym 4 133 (1993); 5 1473 (1994)
JOC 60 3940 (1995)
- cat $K_2OsO_2(OH)_4$, $K_3Fe(CN)_6$, cat 2,3-diphenyl-5,8-bis(9-*O*-dihydroquinine)-pyrazino[2,3-*d*]pyridazine, K_2CO_3 (chiral) JOC 60 3940 (1995)
- cat OsO_4 , $K_3Fe(CN)_6$, cat 2,5-diphenyl-4,6-bis(9-*O*-dihydroquinidine)pyrimidine, K_2CO_3 , $MeSO_2NH_2$ (chiral) JOC 58 3785 (1993); 59 6895 (1994)
JACS 115 8463 (1993)
TL 36 6603 (1995)
- cat OsO_4 , $K_3Fe(CN)_6$, cat 2,5-diphenyl-4,6-bis(9-*O*-dihydroquinine)pyrimidine, K_2CO_3 , $MeSO_2NH_2$ (chiral) JACS 115 8463 (1993)
JOC 59 6895 (1994)
TL 36 4529, 6603 (1995)
- cat OsO_4 , $K_3Fe(CN)_6$, cat 2,5-bis(9-*O*-dihydroquinidine)pyrazine, K_2CO_3 (chiral) JACS 115 3828 (1993)

cat OsO ₄ or K ₂ OsO ₄ , K ₃ Fe(CN) ₆ cat 3,6-bis(9- <i>O</i> -dihydroquinidine)pyridazine, K ₂ CO ₃ (chiral)	JACS 115 3828 (1993); 116 12109 (1994) TL 34 5995 (1993); 35 543, 6427 (1994); 36 3481 (1995)
cat K ₂ OsO ₄ , K ₃ Fe(CN) ₆ , cat 3-(9- <i>O</i> -dihydroquinidine)-6-(2,2-dimethyl-1-(4-anthracenyl)-propyl)pyridazine, K ₂ CO ₃ , MeSO ₂ NH ₂ (chiral)	TL 35 6427 (1994) JACS 117 10817 (1995)
cat K ₂ OsO ₄ or OsO ₄ (?), K ₃ Fe(CN) ₆ , cat 3,6-(9- <i>O</i> -bis-dihydroquinidine)pyridazine-polymer (chiral)	TL 35 6559 (1994)
cat OsO ₄ , K ₃ Fe(CN) ₆ , cat bis(quinidine)-pyridazine macrocycle, K ₂ CO ₃ , MeSO ₂ NH ₂ (chiral)	JACS 115 12579 (1993)
cat OsO ₄ , K ₃ Fe(CN) ₆ , cat dihydroquinidine <i>p</i> -chlorobenzoate, K ₂ CO ₃ (chiral)	TL 31 2999 (1990); 32 3965 (1991); 33 3363 (1992)
cat OsO ₄ , K ₃ Fe(CN) ₆ , cat dihydroquinine <i>p</i> -chlorobenzoate, K ₂ CO ₃ (chiral)	TL 33 3363 (1992); 34 7075 (1993)
cat OsO ₄ , K ₃ Fe(CN) ₆ , cat dihydroquinine terephthalate, K ₂ CO ₃ (chiral)	TL 33 5113 (1992); 35 543 (1994)
cat OsO ₄ , K ₃ Fe(CN) ₆ , cat	TL 33 5081 (1992)
 , K ₂ CO ₃ (chiral)	
cat OsO ₄ , NMO or K ₃ Fe(CN) ₆ , alkaloid polymer (chiral)	TL 31 3003 (1990)
cat OsO ₄ , NMO or K ₃ Fe(CN) ₆ , quinine <i>p</i> -chlorobenzoate polymer (chiral)	Tetr 50 11321 (1994)
cat OsO ₄ , NMO or K ₃ Fe(CN) ₆ , 9- <i>O</i> -phenanthryldihydroquinidine polymer (chiral)	TL 36 1549 (1995)
cat OsO ₄ , NMO or K ₃ Fe(CN) ₆ , 1,4-bis-(dihydroquinidine)phthalazine polymer (chiral)	TL 36 1549 (1995)
cat OsO ₄ , PhSeOR (R = Me, Ph)	TL 22 2051 (1981)
cat OsCl ₃ , K ₃ Fe(CN) ₆ , cat quinuclidine, K ₂ CO ₃ , MeSO ₂ NH ₂ (chiral)	TL 36 1719 (1995)
NBS, H ₂ O or <i>m</i> -ClC ₆ H ₄ CO ₂ H-HBr / NCCH ₂ CO ₂ H, TsCl, py / NaH / H ₃ O ⁺ / K ₂ CO ₃ , MeOH	TL 23 4217 (1982)
I ₂ , AgOAc, H ₂ O, HOAc / KOH	JACS 80 209 (1958) JCS 770 (1963)
I ₂ , AgOAc, H ₂ O, HOAc / LiAlH ₄	JCS C 1327 (1966)
I ₂ , KIO ₃ , HOAc / KOH	TL 4485 (1973)

I_2 , $TiOAc$, $HOAc/H_2O$, $\Delta/NaOH$

Org Syn 59 169 (1980)

Org Syn Coll Vol 6 348 (1988)

trans hydroxylation

I_2 , $TiOAc$, $HOAc/NaOH$

Org Syn 59 169 (1980)

Org Syn Coll Vol 6 348 (1988)

I_2 , AgO_2CPh/KOH

Org Rxs 9 350 (1957) (review)

RCO_3H/H_3O^+

Org Rxs 7 378 (1953) (review)

HCO_2H , H_2O_2 , H_2O

JCS 3634 (1950)

Org Syn Coll Vol 3 217 (1955)

Syn 449 (1979)

CF_3CO_3H , $(Et_3NH)O_2CCF_3/HCl$

JACS 76 3472 (1954)

$HO_2CCH_2CH_2CO_3H$, H_2O

BSCF 2800 (1963)

$KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, H_2O

JOC 56 7022 (1991)

$KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, $HOAc$, H_2SO_4 , H_2O

JOC 25 1901 (1960)

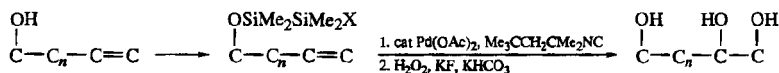
unknown stereochemistry

Aspergillus niger (chiral)

JOC 54 4686 (1989)

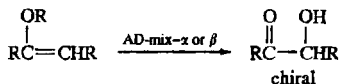
H_2O_2 , H_2WO_4

JOC 58 3980 (1993)

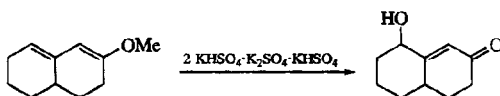


$n=0, 1$; $X=O-t-Pr, Ph$

JACS 113 3987 (1991); 115 6487 (1993); 117 9608 (1995)

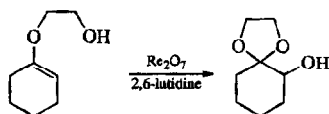


JOC 57 5067 (1992)

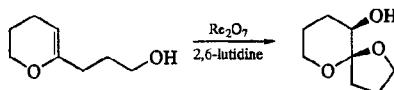


TL 22 4201 (1981)

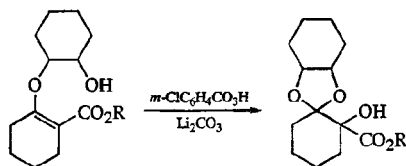
JOC 57 902 (1986); 59 311 (1994)



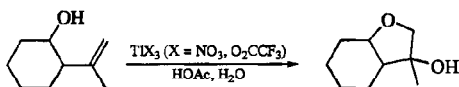
TL 33 7823 (1992)



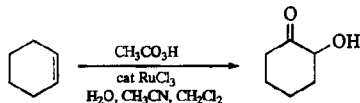
TL 35 5133 (1994)



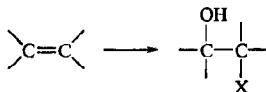
TL 35 3103 (1994)



TL 35 1497 (1994)



JOC 58 2929 (1993)

XReagent(s)

halogen

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See page 638, Section 4.

OAc

I₂, AgOAc, H₂O, HOAc
NaBO₃·4H₂O, Ac₂O, H₂SO₄JACS 109 6403 (1987)
TL 29 2967 (1988)

NHPh

PhNH₂, HgO·2HBF₄

Syn 376 (1981)

NHR

O₃Os=NR/NaHSO₃ or LiAlH₄JACS 97 2305 (1975)
JOC 43 2628 (1978)NR₂R₂NH, Hg(O₂CCF₃)₂/NaBH₄,
O₂TL 31 1683 (1990)
See also page 761, Section 3.NHCO₂RRO₂CNCINa, AgNO₃, H₂O, cat
OsO₄JACS 100 3596 (1978)
Org Syn Coll Vol 7 223 (1990)
SL 615 (1990)

NHTs

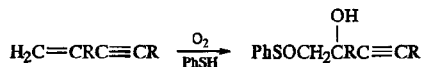
TsNClNa·3H₂O, cat OsO₄JOC 41 177 (1976); 43 2544
(1978)
Org Syn Coll Vol 7 375 (1990)
SL 615 (1990)

PhSe



TL 35 1781 (1994)

TL 36 2327 (1995)

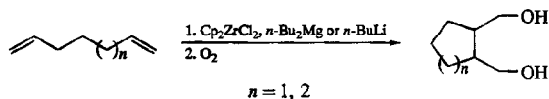


TL 33 5917 (1992)

2. Dienes

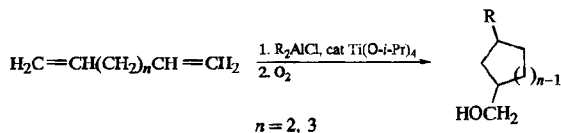


See page 1073, Section 1.

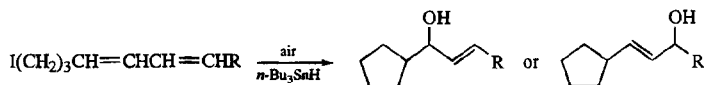


JACS 113 6268 (1991); 116 1845 (1994)

TL 33 7735 (1992); 36 6639 (1995)



JACS 116 8404 (1994)

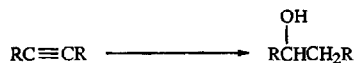
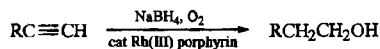


JACS 113 8980 (1991)



TL 33 6779 (1992)

3. Alkynes



JOC 52 2555 (1987)

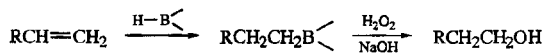
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 Organomet Chem Syn 1 305 (1972) (alkylation of halo compounds)
 Angew Int 11 692 (1972) (free radical reactions)
 H. C. Brown, "Boranes in Organic Chemistry," Cornell Univ. Press, Ithaca, New York (1972)
 G. M. L. Cragg, "Organoboranes in Organic Synthesis," Marcel Dekker, New York (1973)
 See also Intra-Science Chemistry Reports (1973)

1. Hydroboration-Oxidation

See also page 991, Section 1.



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


- H. C. Brown, "Hydroboration," W. A. Benjamin, New York (1962)
 Org Rxs 13 1 (1963)
 TL 26 2187 (1985) (ultrasound enhancement); 30 1483 (NaBO₃·4H₂O oxidation), 5105
 (Na₂CO₃·3/2H₂O₂ oxidation) (1989)
 JOC 51 445 (1986) (cyclic dienes); 54 5930 (1989) (sodium perborate oxidation)
 Chem Rev 91 1179 (1991) (transition metal-promoted)
 D. A. Evans and G. C. Fu in "Advances in Catalytic Processes," Ed. M. P. Doyle, JAI Press, London
 (1995), Vol 1 (catalytic)

BH₃·THF

JACS 82 4708 (1960); 83 2544 (1961); 88
 5851 (1966)
 Org Syn Coll Vol 6 919 (1988)
 JOC 56 1027, 1670 (1991); 59 2025 (1994)
 TL 33 4115, 5887 (1992); 35 223 (1994)
 SL 696 (1993)

BH₃·SMe₂

JOC 39 1437 (1976); 42 1392 (1977); 56 1670
 (1991); 59 2025 (1994)
 Org Prep Proc Int 13 225 (1981) (review)
 Org Syn Coll Vol 6 719 (1988)

$\text{BH}_3\text{-S} \begin{array}{c} \diagup \text{O} \diagdown \end{array}$	JOC 57 4970 (1992)
MeBH_2	JOC 51 4925 (1986); 55 5051 (1990)
RBH_2 (R = Me, <i>i</i> -Pr, <i>n</i> -Bu, <i>s</i> -Bu, <i>t</i> -Bu)	JOC 54 6085 (1989)
$\text{Me}_2\text{CHCMe}_2\text{BH}_2$	JACS 85 2066 (1963); 89 5475 (1967) JOC 54 1978 (1989) TL 32 1479 (1991)
Me_2BH	JOC 51 4925 (1986)
9-BBN	JACS 96 7765 (1974) JOC 44 2328 (1979); 46 4599 (1981); 50 5583 (1985); 56 1020, 1027 (1991) TL 29 2077 (1988); 30 5857, 5861 (1989)
(Sia) ₂ BH	JACS 83 1241 (1961); 84 190 (1962) (dienes) Org Syn 64 164 (1985) Org Syn Coll Vol 6 919 (1988); 7 258 (1990)
	JACS 106 3768 (1984)
$\text{Me}_2\text{CHCMe}_2\text{BHCl}\cdot\text{SMe}_2$	JOC 45 4540 (1980); 47 863, 872 (1982)
$\text{H}_2\text{BCl}\cdot\text{OEt}_2$	JOC 38 182 (1973) JACS 98 1785 (1976)
$\text{H}_2\text{BCl}\cdot\text{SMe}_2$	JOC 42 2533 (1977); 44 2417 (1979); 51 895 (1986)
$\text{H}_2\text{BBr}\cdot\text{SMe}_2$	Syn 695 (1977) JOC 44 2417 (1979); 51 895 (1986)
$\text{H}_2\text{BI}\cdot\text{SMe}_2$	JOC 44 2417 (1979); 51 895 (1986)
$\text{HBCl}_2\cdot\text{OEt}_2$	JACS 98 1798 (1976)
$\text{HBCl}_2\cdot\text{SMe}_2$	JOC 42 2533 (1977); 45 384 (1980)
$\text{HBBr}_2\cdot\text{SMe}_2$	JOC 45 384 (1980); 53 4811 (1988)
$\text{HBI}_2\cdot\text{SMe}_2$	JOC 45 384 (1980)
	JOC 42 3243 (1977)
	Syn 214 (1981)
CB	JACS 93 1816 (1971); 97 5249 (1975) Tetr 32 981 (1976)
CB, cat LiBH_4	CC 205 (1991) JOC 60 5316 (1995)
CB, cat $\text{CIRh(PPh}_3)_3$	Angew Int 24 878 (1985) JACS 110 6917 (1988); 113 6139 (1991); 114 6671, 6679, 8863, 9350, 9434 (1992) TL 30 5857 (1989); 34 8513 (1993); 35 2435 (1994) JOC 55 2280, 5192 (1990); 56 1670 (1991) SL 893 (1995)

CB, cat $[\text{Rh}(\text{COD})\text{Cl}]_2-4\text{PPH}_3$

TL 30 395, 5857, 5861 (1989); 33 5887 (1992)

JOC 56 1020, 1027, 2949 (1991)

JACS 113 6139 (1991)

CB, cat $[\text{Rh}(\text{COD})\text{Cl}]_2$ -diphosphines

TL 30 5857 (1989); 35 1421 (1994)

CB, cat $[\text{Rh}(\text{COD})(\text{dppb})]\text{BF}_4$

JACS 114 8863 (1992)

CB, cat $[\text{Rh}(\text{NBD})(\text{dppb})]\text{BF}_4$

JACS 114 6671 (1992)

CB, cat $[\text{Rh}(\eta^3\text{-2-Me-allyl})i\text{-Pr}_2\text{PCH}_2\text{CH}_2\text{P}(i\text{-Pr})_2]$

JACS 114 8863 (1992)

CB, cat $[\text{Rh}(\text{COD})\text{Cl}]_2-4\text{P}(\text{OEt})_3$

TL 30 5857 (1989)

CB, cat $[\text{Ir}(\text{COD})(\text{PCy}_3)\text{py}]\text{PF}_6$

JACS 113 4042 (1991); 114 6671 (1992)

CB, cat $(\text{Me}_3\text{C}_3)_2\text{LaR}$ [R = H or $\text{CH}(\text{SiMe}_3)_2$]

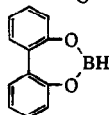
JACS 114 9220 (1992)

CB, cat $\text{Nb}(1,3,5\text{-Me}_3\text{C}_6\text{H}_3)_2$

TL 34 6813 (1993)

CB; cat MI_3 (M = Sm, Nb, Sc, Pr, Lu) or
 $\text{SmI}_2(\text{O-}i\text{-Bu})$ or $\text{Sm}(\text{O-}i\text{-Pr})_3$ or $\text{Eu}(\text{tfc})_3$ or

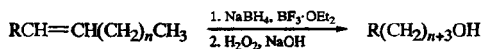
JOC 58 5307 (1993)



Heterocycles 32 425 (1991)

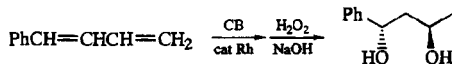


JOC 57 3482 (1992)

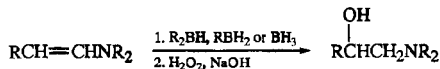


TL 33 2419 (1992)

JACS 117 12683 (1995)

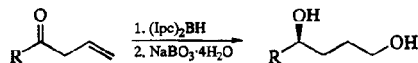


TL 32 3387 (1991)

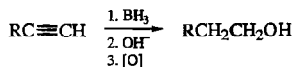


TL 34 7693 (1993) (chiral); 35 3251, 5165 (1994)

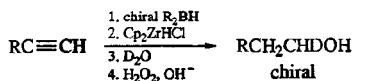
JOC 60 2026 (1995)



JOC 59 2676 (1994)



JACS 89 291 (1967)



TL 35 6247 (1994)

1.1. Asymmetric Hydroboration

Reviews:

Tetr 37 3547 (1981)

H. C. Brown, P. K. Jadhav in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Vol 2, Chpt 1

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vols E21d (p 4396) and E21e (p 4519), G. Thieme, Stuttgart-New York (1995)

IpcBH₂

JACS 99 5514 (1977); 106 1797 (1984)

JOC 46 5047 (1981); 52 310 (1987); 54 6085 (1989)



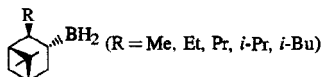
JOC 53 5513 (1988)



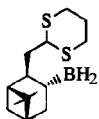
TL 35 4715 (1994)



JOC 55 1217 (1990); 59 2365 (1994)



JOC 59 2365 (1994)



JOC 55 2855 (1990)

(Ipc)₂BH

JACS 83 486 (1961); 86 397, 1071, 1076 (1964); 95 532, 7171 (1973); 99 5514 (1977); 108 2049 (1986)

Tetr 24 6365 (1968)

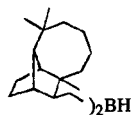
TL 1133 (1970)

Israel J Chem 15 12 (1977)

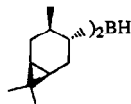
JOC 47 5065 (1982); 53 1903 (1988); 57 504 (1992)

Org Syn 63 44 (1984)

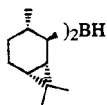
Org Syn Coll Vol 7 339 (1990)



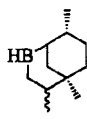
JOC 46 2988 (1981)



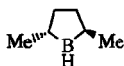
JOC 53 2911 (1988)



JOC 53 2911 (1988)



Heterocycles 18 169 (1982)



JACS 107 4549 (1985)

CB, cat [RhCl(COD)]₂, cat diopJOC 53 5178 (1988); 56 1670 (1991)
Tetr Asym 2 613 (1991)CB, cat [RhCl(COD)]₂, cat BINAPJOC 53 5178 (1988); 56 1670 (1991)
Tetr Asym 2 613 (1991)CB, cat [RhCl(COD)]₂, cat various chiral
diphosphines

Tetr Asym 2 613 (1991)

CB, cat [RhCl(C₂H₄)₂]₂, cat various chiral
diphosphines

TL 31 231 (1990)

CB, cat [Rh(COD)₂]BF₄, cat BINAP

JACS 111 3426 (1989)

CB, cat [Rh(COD)₂]BF₄, cat Josiphos

JACS 116 4062 (1994)

2. Carbonylation and Related Reactions



Organoborane

R₃B

Reagents

 $\text{CH}_2\text{SMe}_2^+ / [\text{O}]$

CC 505 (1967)

CO, NaBH₄ / OH⁻

JACS 89 2740 (1967)

CO, MHBR₃ (M = Li, Na, K) /
OH⁻

JOC 44 467 (1979)

CO, LiAl(OMe)₃ / OH⁻

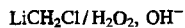
JACS 91 2144 (1969)

CO, LiAl(OMe)₃ / LiAlH₄ / [O]

JOC 45 4067 (1980)

CO, KHB(O-*i*-Pr)₃ / OH⁻

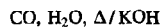
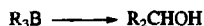
Syn 701 (1979)



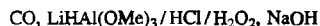
Heterocycles 28 283 (1989)

TL 34 7845 (1993)

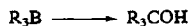
(R = alkyl, vinylic)



JACS 89 2738 (1967)



Syn 676 (1978)



JACS 89 2737, 5478 (1967); 90 5283 (1968); 91 1224, 1226 (1969); 92 2460, 6648 (1970); 93 1818 (1971)

JOMC 26 C67 (1971)

Syn 197 (1972)

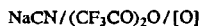
CC 607 (1979)

Tetr 37 2441 (1981)

JOC 51 4925 (1986); 55 3697, 5051 (1990)

TL 28 3771 (1987)

Org Syn Coll Vol 7 427 (1990)

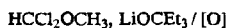


CC 1048 (1971); 186 (1973)

JCS Perkin I 653 (1981)



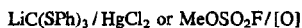
JACS 93 2070 (1971)



JOC 38 2422, 3968 (1973)

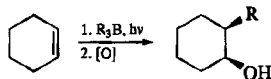
Angew Int 20 1038 (1981)

Organomet 1 212 (1982)

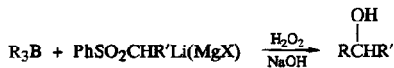


CC 1149 (1981)

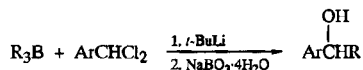
3. Other Reactions



Tetr 29 2365 (1973)



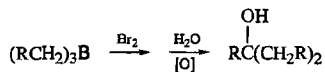
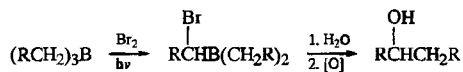
BSCF II 99 (1981)



TL 36 8545 (1995)



JOC 59 5530 (1994)



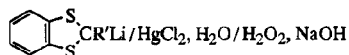
JACS 93 1025, 2796 (1971)

Syn 303, 304 (1972)

JOC 44 2417 (1979)

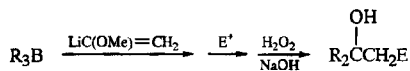
LiCR'(SPh)₂/HgCl₂, H₂O/H₂O₂, NaOH

CC 863 (1974)



JCS Perkin I 1172 (1977)

TL 1895 (1979)

E⁺ = HCl, R'X

JOMC 156 123 (1978)

7. ETHER CLEAVAGE

Reviews:

Chem Rev 54 615 (1954); 59 737 (1959) (epoxides)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol 6/3, G. Thieme, Stuttgart (1965), p 143

"The Chemistry of the Ether Linkage," Ed. S. Patai, Interscience, New York (1967), pp 21-80
Syn 249 (1983); 629 (1984) (epoxides)

Pure Appl Chem 55 589 (1983) (chiral 2,3-epoxy alcohols)

1. Cleavage of Acyclic Ethers



Reviews:

Chem Rev 54 615 (1954)

Adv Carbohydr Chem 12 137 (1957) (hydrogenolysis)

See also page 685, Section 7.

Reagent(s)	R	R'	
H ₂ , cat Raney Ni	1°, 2°, 3° alkyl; aryl	benzylic	Org Rxn 7 263 (1953) Methods Carbohydr Chem 6 378 (1972)
H ₂ , cat Ni ₂ B	2° alkyl	(<i>p</i> -NO ₂ C ₆ H ₄) ₂ CH	JOC 53 1030 (1988)
H ₂ , cat Pd-C	aryl 1°, 2° alkyl	2,4-Me ₂ C ₆ H ₃ CH ₂ PhCH ₂	Syn 987 (1982) CC 1234 (1980) JOC 47 1373 (1982); 53 1218, 1823 (1988); 54 5153 (1989)
H ₂ , cat Pd(OH) ₂ -C	1°, 2° alkyl	PhCH ₂	JOC 54 4643 (1989); 60 2570 (1995)
H ₂ , cat PtO ₂	1°, 2°, 3° alkyl	(<i>p</i> -NO ₂ C ₆ H ₄) ₂ CH	JOC 53 1030 (1988)


Reagent(s)	R	R'	
cat PdO·xH ₂ O, cyclohexene, EtOH	1° alkyl	PhCH ₂	JOC 55 5535 (1990)
cat Pd(OH) ₂ , C, cyclohexene	1°, 2° alkyl	PhCH ₂	Syn 396 (1981) TL 28 4131 (1987)
HCO ₂ H, cat Pd-C	1°, 2° alkyl	PhCH ₂	Carbohydr Res 83 175 (1980) JOC 58 6114 (1993)
HCO ₂ H, cat Pd(OAc) ₂ , cat PPh ₃ , Et ₃ N	aryl	CH ₂ CH=CH ₂	JOC 56 6083 (1991)
(NH ₄) ₂ O ₂ CH, cat Pd-C, MeOH or CH ₃ COCH ₃	1°, 2° alkyl	PhCH ₂ , Ph ₃ C	Syn 76 (1985) JOC 59 3123 (1994)
(NH ₄) ₂ O ₂ CH, cat Pd-C, MeOH, HOAc	serine or threonine	PhCH ₂	Syn 929 (1980)
N ₂ H ₄ , H ₂ O, cat Pd-C	1°, 2° alkyl	PhCH ₂	Syn 317 (1986) TL 28 6381 (1987)
Li(4- <i>t</i> -BuC ₆ H ₄) ₂	1° alkyl, 2° allylic	PhCH ₂	IACS 110 854 (1988); 113 8791 (1991)
Li, NH ₃	1°, 2° alkyl	PhCH ₂	JOC 53 4877 (1988) TL 36 799 (1995)
Na, NH ₃	aryl 1°, 2° alkyl	alkyl PhCH ₂	JCS 102 (1947) JOC 29 1787, 3725 (1964); 34 97 (1969); 54 3374 (1989); 57 2575 (1992)
	1° alkyl	<i>p</i> -MeOC ₆ H ₄ (Ph) ₂ C	JOC 56 3102 (1991)
Na-K	aryl	PhCH ₂	JOC 30 1610 (1965)
K, toluene, crown ether / <i>i</i> -PrOH	aryl	Me	TL 33 5555 (1992)
Ca, NH ₃	1°, 2° alkyl	PhCH ₂	TL 36 799 (1995)
NaBH ₄ , cat Pd(PPh ₃) ₄	aryl	CH ₂ CH=CH ₂	TL 35 4349 (1994)
NaBH ₃ CN, BF ₃ ·OEt ₂	1°, 2° alkyl; aryl	<i>p</i> -MeOC ₆ H ₄ CH ₂	JOC 60 5961 (1995)
LiHBEt ₃	aryl	Me	TL 35 8727 (1994)
LiH(<i>sec</i> -Bu) ₃	aryl	Me	TL 35 8727 (1994)
<i>i</i> -Bu ₂ AlH or <i>i</i> -Bu ₃ Al	aryl	Me	Syn 617 (1975)
LiAlH ₄ , C ₆ H ₆	aryl	Me	CC 507 (1980)
LiAlH ₄ , CCl ₄ , THF	3° alkyl	Me	JOC 51 1620 (1986)
PhSiH ₃ , cat Pd(PPh ₃) ₄	aryl	CH ₂ CH=CH ₂	TL 36 5441 (1995)

$n\text{-Bu}_3\text{SnH}$, cat $\text{PdCl}_2(\text{PPh}_3)_2$	aryl	$\text{CH}_2\text{CH}=\text{CH}_2$	JACS 111 8912 (1989)
$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{PPh}_3)_4$, HOAc	aryl	$\text{CH}_2\text{CH}=\text{CH}_2$	TL 36 3933 (1995)
$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{PPh}_3)_4$, ZnCl_2	aryl	$\text{CH}_2\text{CH}=\text{CH}_2$	JOC 57 644 (1992)
$\text{py}\cdot\text{HCl}$	aryl	Me	JOC 54 1485 (1989)
HCl	aryl 2° alkyl	MeOCH ₂ <i>t</i> -Bu	JACS 104 5551 (1982) JOC 53 937 (1988)
HBr, HOAc	aryl	Me	JACS 109 3098 (1987)
HBr, NaI	aryl	Me	TL 34 5393 (1993)
HOAc, H ₂ O	1° alkyl aryl	(<i>p</i> -MeOC ₆ H ₄) ₂ (Ph)C MeOCH ₂	SL 83 (1993) J Med Chem 9 1 (1965)
CF ₃ CO ₂ H	aryl 1°, 2° alkyl 2° alkyl	MeOCH ₂ CH ₂ OCH ₂ <i>p</i> -MeOC ₆ H ₄ CH ₂ <i>t</i> -Bu	JACS 100 8031 (1978) SL 523 (1995) JOC 53 937 (1988)
CF ₃ CO ₂ H, (CF ₃ CO) ₂ O	1° alkyl	Ph ₃ C	TL 34 1713 (1993)
CF ₃ CO ₂ H, cat RhH(PPh ₃) ₄	2° alkyl	$\text{CH}_2\text{CH}=\text{CH}_2$	JOC 55 3691 (1990)
BF ₃ ·OEt ₂ , <i>n</i> -Bu ₄ NI	1°, 2° alkyl; aryl	Me, PhCH ₂ , $\text{CH}_2\text{CH}=\text{CH}_2$	Syn 274 (1985)
BF ₃ ·OEt ₂ , SMe ₂	1°, 2° alkyl; aryl	PhCH ₂	Chem Pharm Bull 28 3662 (1980) CC 1802 (1987) TL 36 7023 (1995)
BF ₃ ·OEt ₂ , RSH	1°, 2° alkyl; aryl	Me, PhCH ₂	JCS Perkin I 2237 (1976); 611 (1977) CL 97 (1979) JOC 44 1661 (1979) Chem Pharm Bull 28 3662 (1980)
BF ₃ ·OEt ₂ , PhSH	2° alkyl	MeOCH ₂	JACS 100 1938 (1978)
BF ₃ ·OEt ₂ , HSCH ₂ - CH ₂ SH, HCl	2° alkyl	Me	JACS 106 3539 (1984); 111 6287 (1989)
BF ₃ ·SMe ₂	aryl	Me	JOC 54 1485 (1989)
BCl ₃	aryl 2° alkyl	Me PhCH ₂	JCS 2929 (1960) TL 4153 (1966) JOC 60 5316 (1995)
BCl ₃ , SMe ₂	1°, 2° alkyl	PhCH ₂	SL 663 (1993)
BX ₃ ·SMe ₂ (X = Cl, Br)	aryl	Me, CH ₂	TL 21 3731 (1980)

Reagent(s)	R	R'	
BBr ₃	1°, 2° alkyl; aryl	1°, 2° alkyl; PhCH ₂	JACS 64 1128 (1942); 111 7932 (1989)
	aryl	PhCH ₂	JCS 2929 (1960) Chem Ind 1658 (1963) Tetr 24 2289 (1968) JOC 41 170 (1976); 44 4444 (1979); 51 1620 (1986); 55 4478 (1990); 57 1262 (1992) J Med Chem 20 164 (1977); 24 773 (1981) Syn Commun 9 341, 407 (1979)
BBr ₃ , NaI, 15-crown-5	1°, 2° alkyl	Me	TL 22 4239 (1981)
BI ₃	aryl	Me	Syn Commun 9 341 (1979)
BI ₃ ·PhNEt ₂	aryl	Me	TL 31 6977 (1990)
Me ₂ BBr	1°, 2° alkyl; aryl 1°, 2°, 3° alkyl	Me, PhCH ₂ MeOCH ₂ , MeOCH ₂ - CH ₂ OCH ₂ , MeSCH ₂ - p-MeOC ₆ H ₄ CH ₂	TL 24 2969 (1983) TL 24 3969 (1983) JOC 49 3912 (1984) JOC 57 1777 (1992)
Ph ₂ BBr	1° alkyl 2° alkyl	EtOCH ₂ , MeOCH ₂ - CH ₂ OCH ₂ MeOCH ₂	TL 24 3969 (1983) JOC 49 3912 (1984) JOC 55 4860 (1990)
AlCl ₃ ·PhNMe ₂	1°, 2° alkyl; aryl	PhCH ₂ , CH ₂ CH=CH ₂	TL 32 1321 (1991)
AlCl ₃ , n-Bu ₄ NI	2° alkyl	Me	TL 32 5593 (1991) SL 831 (1991)
AlCl ₃ , NaI	1°, 2° alkyl	Me	TL 35 3367 (1994)
AlX ₃ (X = Cl, Br), EtSH	1°, 2° alkyl; aryl	Me, CH ₂	CL 97 (1979) JOC 45 4275 (1980); 59 5414 (1994)
R ₂ AlCl (R = Et, i-Bu)	1° alkyl	Ph ₃ C	TL 23 2641 (1982)
AlI ₃	aryl	1°, 2° alkyl	Syn 249 (1983) JACS 117 11906 (1995)
cat t-BuMe ₂ SiOTf	1° alkyl	3° alkyl	TL 36 711 (1995)
Me ₃ SiSR (R = Me, Ph), ZnI ₂ , n-Bu ₄ NI	1°, 2° alkyl; aryl	Me, PhCH ₂	TL 21 2305 (1980)
H ₂ SiI ₂	1° alkyl, aryl	Me	JOC 52 4846 (1987)
SiCl ₄ , NaI	1°, 2° alkyl; aryl	1°, 2° alkyl; PhCH ₂ ; CH ₂ CH=CH ₂	Syn 1048 (1982)

MeSiCl ₃ , NaI	1°, 2° alkyl	Me, Et, PhCH ₂ , Ph ₃ C, THP	Angew Int 20 690 (1981) JOC 48 3667 (1983); 55 1569 (1990)
Me ₃ SiCl, NaI	1°, 2° alkyl; aryl	Me, Et, PhCH ₂ , Ph ₃ C	CC 874 (1978) JOC 44 1247 (1979) Ann 1416 (1983) Chem Ind 34 (1984) TL 25 1429 (1984)
	1°, 2°, 3° alkyl; benzylic; allylic	MeOCH ₂ CH ₂	TL 25 1429 (1984)
Me ₃ SiCl, cat SnCl ₂ , PhOMe	1°, 2° alkyl	<i>p</i> -MeOC ₆ H ₄ CH ₂	SL 415 (1992)
Me ₃ SiI	1°, 2° alkyl; aryl	Me, <i>t</i> -Bu	Angew Int 15 774 (1976) JOC 42 3761 (1977); 44 4444 (1979) Org Syn 59 35 (1980) CC 876 (1987) Org Syn Coll Vol 6 353 (1988) TL 35 3367 (1994)
(Me ₃ Si) ₂ , I ₂	2° alkyl, aryl	Me, PhCH ₂ , Ph ₃ C	Angew Int 18 612 (1979) Ann 1416 (1983)
PhSiMe ₃ , I ₂	aryl	1° alkyl, PhCH ₂	Syn 417 (1977)
SnCl ₄	2° alkyl	PhCH ₂	JOC 54 1346 (1989)
P ₂ I ₄	aryl	MeOCH ₂ , MeOCH ₂ - CH ₂ , Me ₃ SiCH ₂ - CH ₂ OCH ₂	TL 27 1607 (1986)
TiCl ₃ , Mg	1°, 2° alkyl; aryl 1° alkyl, aryl	PhCH ₂ , CH ₂ CH=CH ₂ HC≡CCH ₂	TL 33 5129 (1992) SL 581 (1993)
TiCl ₄	1°, 2° alkyl	<i>t</i> -Bu	JACS 104 1116 (1982) JOC 59 7937 (1994)
	2° alkyl aryl	PhCH ₂ PhCH ₂	JOC 54 1346 (1989) JOC 58 3877 (1993)
TiCl ₄ or ZnBr ₂	2°, 3° alkyl; allylic; aryl	MeOCH ₂ CH ₂ OCH ₂	TL 809 (1976) JACS 100 8034 (1978)
Cp ₂ ZrCl ₂ , <i>n</i> -BuLi	1°, 2° alkyl	CH ₂ CH=CH ₂	JOC 58 774 (1993)
FeCl ₃	1°, 2° alkyl	ArCH ₂	TL 28 3823 (1987)
PdCl ₂ , CuCl, O ₂ , H ₂ O, DMF	2° alkyl	CH ₂ CH=CH ₂	TL 34 6929 (1993)
cat PdCl ₂ , CuCl, O ₂ , H ₂ O, DMF	2° alkyl	isopropenyl	TL 34 6929 (1993)

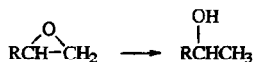
Reagent(s)	R	R'	
HgCl ₂ or AgNO ₃ , H ₂ O	1° alkyl, 1° allylic, 1° benzylic	MeSCH ₂	TL 3269 (1975)
<i>n</i> -Bu ₄ NF	1°, 2° alkyl; allylic; aryl	Me ₃ SiCH ₂ CH ₂ OCH ₂	TL 21 3343 (1980)
LiI, 2,4,6-collidine	aryl	Me	CC 616 (1969)
NaNH ₂ , piperidine	aryl	1° alkyl, PhCH ₂	Chem Ind 80 (1957)
PhNMeNa, HMPA	aryl	Me	Syn 638 (1980)
NaCN, DMSO	aryl	Me	TL 5183 (1978)
MeMgI	aryl	Me	JACS 70 4127 (1948); 117 12683 (1995) TL 31 3325 (1990)
Na ₂ S, NMP	aryl	Me	JACS 98 3237 (1976)
Na ₂ S, Me ₃ SiCl	aryl	Me	JOC 58 4742 (1993)
<i>n</i> -BuSH, MgBr ₂	1°, 2°, 3° alkyl	MeOCH ₂ , MeSCH ₂ , Me ₃ SiCH ₂ CH ₂ - OCH ₂ , MeOCH ₂ - CH ₂ OCH ₂	SL 183 (1991)
MeSLi, DMF	aryl	Me	TL 3859 (1977) JACS 101 1353 (1979) JOC 45 4407 (1980)
MeSNa, DMF or HMPA	aryl	9-anthrylmethyl	JACS 96 590 (1974)
EtSNa, DMF	aryl	Me	TL 1327 (1970) Austral J Chem 25 1719, 1731 (1972) JACS 98 3237 (1976); 108 1311, 2662, 3040 (1986) JOC 43 2553 (1978); 52 1072 (1987); 60 739 (1995) Org Syn Coll Vol 6 567 (1988)
<i>n</i> -PrSNa, DMF	aryl	Me	JOC 42 2569 (1977); 56 2081 (1991) TL 28 4015 (1987)
<i>n</i> -PrSLi, HMPA	aryl	Me	TL 4459 (1970)
<i>n</i> -BuSLi, HMPA	aryl	Me	TL 505 (1977)
<i>t</i> -BuSLi, HMPA	aryl	Me	JACS 107 2712 (1985)
PhSLi, HMPA	aryl	Me	TL 27 2687 (1986)
<i>p</i> -MeC ₆ H ₄ SNa, HMPA	aryl	Me, PhCH ₂	Syn 191 (1976)


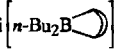
Me ₃ SiSNa	aryl	Me	JOC 55 5987 (1990)
PhCH ₂ SeNa, DMF	aryl	Me	JOC 42 1228 (1977)
Ph ₂ PLi	aryl	Me, PhCH ₂ , CH ₂ CH=CH ₂	Chem Ind 1386 (1964) JCS 4120 (1965) TL 1071 (1976) JACS 107 7967 (1985) Org Syn Coll Vol 6 567 (1988)
	3° alkyl	Me	TL 33 4225 (1992)
(CF ₃) ₂ CHOH	1° alkyl	(<i>p</i> -MeOC ₆ H ₄) ₂ (Ph)C	TL 36 7833 (1995)
<i>t</i> -BuO ₂ H, cat Cr-pillared montmorillonite	1° alkyl	PhCH ₂	JOC 57 5841 (1992)
DDQ, H ₂ O	1° alkyl 1°, 2° alkyl 1° alkyl or allylic, 2° alkyl	4-N ₃ C ₆ H ₄ CH ₂ 4-(CH ₃) ₃ CCONH-C ₆ H ₄ CH ₂ 4-MeOC ₆ H ₄ CH ₂ or 3,4-(MeO) ₂ C ₆ H ₃ CH ₂	TL 32 3557 (1991) TL 32 4019 (1991) TL 23 885 (1982); 28 5125 (1987) JACS 112 7001 (1990) SL 660 (1994)
AgO, HNO ₃	1° alkyl	<i>p</i> -MeOC ₆ H ₄	JOC 58 4945 (1993)
CAN, H ₂ O, CH ₃ CN	1°, 2° alkyl	<i>p</i> -MeOC ₆ H ₄	CC 201 (1984) TL 29 1389 (1988)
Br ₂ /H ₂ O, Na ₂ CO ₃ or Ca(OH) ₂	1°, 2° alkyl	PhCH ₂	JOC 33 4292 (1968)
NBS, H ₂ O	1°, 2° alkyl	CH ₂ CH=CH ₂	JOC 59 7928 (1994)
NBS, CaCO ₃ , H ₂ O, CCl ₄ , hv	2° alkyl	PhCH ₂	JOC 55 378 (1990)
I ₂ , MeOH	1°, 2°, 3° alkyl	<i>p</i> -MeOC ₆ H ₄ CH ₂	SL 1157 (1995)
electrolysis	1° alkyl	4-NH ₂ C ₆ H ₄ CH ₂	TL 32 3557 (1991)
electrolysis, cat SmCl ₃	1°, 2° alkyl; 2° allylic; aryl	allylic	TL 33 2485 (1992)
hv, MeOH	aryl	Me	JOC 53 2877 (1988)

2. Reduction of Cyclic Ethers

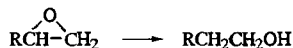
Reviews:

- J. Seyden Penne, "Reductions by the Alumino- and Borohydrides in Organic Synthesis," VCH-Lavoisier (1991), Chpt 1
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 4.4, p 871


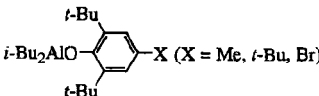


H ₂ , Raney nickel, NaOH	JACS 71 3362 (1949)
(NH ₄)O ₂ CH, cat Pd-C	JOC 60 4922 (1995)
Li, NH ₃	JACS 107 1015 (1985) JOC 51 5450 (1986)
Li, RNH ₂	Quart Rev 12 22-23 (1958)
Li, EDA	JOC 35 3243 (1970); 51 3391 (1986) JACS 92 6914 (1970); 107 1015 (1985)
Li, biphenyl/H ₂ O	Angew Int 25 653 (1986)
Li or Mg, naphthalene/H ₂ O	Angew Int 25 653 (1986)
Mg, CdCl ₂ , H ₂ O	TL 34 1681 (1993)
Ca, EDA	JOC 51 3391 (1986)
CB	JOC 42 512 (1977)
BH ₃ , NaBH ₄	JOC 45 3836 (1980); 54 1295 (1989)
LiBH ₄	JCS C 928 (1970)
LiBH ₄ , MeOH	JOC 51 4000 (1986) TL 36 1621 (1995)
LiH ₃ BN 	JOC 59 6378 (1994)
NaH ₂ B[(OCH ₂ CH ₂) _n OH] ₂ (n = 8, 9)	JOC 52 671 (1987)
LiHBEt ₃	JACS 95 8486 (1973); 106 3252 (1984); 109 8117 (1987); 110 1901 (1988) Angew Int 18 958 (1979) JOC 45 1 (1980) TL 28 4959 (1987)
KHBEt ₃	Bull Korean Chem Soc 8 285 (1987)
KHB(sec-Bu) ₃	Bull Korean Chem Soc 10 382 (1989)
KHBPh ₃	JOC 52 5564 (1987)
Li 	CC 672 (1976)
AlH ₃	JACS 88 1464 (1966); 90 2927 (1988) JOC 32 1748 (1967)
AlH ₃ ·NEt ₃	JOC 58 3974 (1993)
<i>i</i> -Bu ₂ AlH	JOC 50 2443 (1985); 57 1618 (1992) TL 34 3511 (1993)
<i>i</i> -Bu ₂ AlH, <i>i</i> -Bu ₂ AlO- <i>s</i> -Bu	JOC 57 1618 (1992)
ROAlH ₃ (R = <i>i</i> -Pr, <i>i</i> -Bu)	JOC 33 1132 (1968)

$(t\text{-BuO})_2\text{AlH}$	JOC 33 1132 (1968)
LiAlH_4	JACS 70 3738 (1948); 71 1675 (1949); 74 923, 5917 (1952) Org Rxs 6 469 (1951) (review) JOC 32 2873 (1967); 57 86, 1618 (1992); 60 41 (1995) TL 30 2775 (1989)
$\text{LiAlH}_4 \cdot \text{MeN} \begin{array}{c} \diagup \\ \diagdown \end{array}$	TL 35 1515 (1994)
NaAlH_4	JOC 58 4727 (1993)
$\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$	JOC 38 1385 (1973)
$\text{NaH}_2\text{AlEt}_2$	Bull Korean Chem Soc 13 199 (1992)
$\text{NaHAlEt}_2\text{N} \begin{array}{c} \diagup \\ \diagdown \end{array}$	JOC 58 1941 (1993)
$\text{LiHAl}(i\text{-Bu})_2(n\text{-Bu})$	JOC 49 1717 (1984)
$\text{GaH}_3 \cdot \text{PCy}_3$	TL 35 5915 (1994)
LiH_3InPh	TL 36 3169 (1995)
$\text{LiH}_2\text{InPh}_2$	TL 36 3169 (1995)
$n\text{-Bu}_3\text{SnH}$, LiI	Tetr 45 2895 (1989)
$n\text{-Bu}_3\text{SnH}$, NaI	TL 29 819 (1988) Tetr 45 2895 (1989)
$n\text{-Bu}_3\text{SnH}$, MgI_2	Tetr 45 2895 (1989)
$\text{PhSeLi} / n\text{-Bu}_3\text{SnH}$	JACS 111 3374 (1989)
$\text{Na}[\text{PhSeB}(\text{OEt})_3] / n\text{-Bu}_3\text{SnH}$	JACS 111 3728 (1989)
$\text{NaTeH} / \text{Ni boride}$	TL 26 6197 (1985)
MeLi , CuBr , $n\text{-Bu}_3\text{P}$	JACS 112 1286 (1990) (chemoselective)



H_2 , Raney nickel	JACS 71 3362 (1949)
H_2 , cat Pd-C ($\text{R} = \text{Ar}$)	TL 35 8927 (1994)
Li , naphthalene/ H_2O ($\text{R} = \text{Ph}$)	Angew Int 25 653 (1986)
K , biphenyl/ H_2O ($\text{R} = \text{CO}_2\text{Et}$)	Angew Int 25 653 (1986)
Zn , $\text{Me}_3\text{SiCl} / \text{H}_2\text{O}$	Syn Commun 13 869 (1983)
LiH , $t\text{-BuOH}$, $\text{Ni}(\text{OAc})_2$	TL 36 6051 (1995)
BH_3	JOC 32 2873 (1967)
BH_3 , $\text{BF}_3 \cdot \text{OEt}_2$	CC 1549 (1968)
BH_3 , NaBH_4	JACS 90 2686 (1968)

NaBH_3CN , $\text{BF}_3 \cdot \text{OEt}_2$	JOC 46 5214 (1981) TL 27 6071 (1986)
$\text{Zn}(\text{BH}_4)_2$, SiO_2	CC 1334 (1990)
LiH_3BN 	TL 33 4533 (1992)
KHBPh_3 , cat Ph_3B	JOC 52 5564 (1987)
AlH_3	JACS 88 1464 (1966); 90 2927 (1988) JOC 32 1748 (1967)
LiAlH_4 , AlCl_3	JACS 78 3226 (1956); 84 2356 (1962); 90 6495 (1968) Rec Chem Prog 22 129 (1961) JOC 32 1748 (1967) TL 981 (1978); 33 753 (1992)
 $i\text{-Bu}_2\text{AlO}$ $i\text{-Bu}_3\text{Al}$	SL 255 (1991) JOC 57 1618 (1992)
$n\text{-Bu}_3\text{SnH}$, MgI_2	Tetr 45 2895 (1989)
Cp_2TiCl , 1,4-cyclohexadiene	JACS 112 6408 (1990); 116 986 (1994)
SmI_2 , $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$	JACS 117 4722 (1995)



H_2 , cat $\text{Pd}(\text{OH})_2\text{-C}$	TL 32 5273 (1991)
Li , NH_3	BCSJ 52 2640 (1979); 53 2642 (1980)
Li , K or Mg ; naphthalene or biphenyl/ H_2O	Angew Int 25 653 (1986)
$i\text{-Bu}_2\text{AlH}$	JACS 107 1015 (1985) TL 28 2021 (1987); 36 4689 (1995)
LiAlH_4	JOC 59 4131 (1994)
NaSePh , $\text{Ti}(\text{O}-i\text{-Pr})_4$ /Raney Ni	JOC 58 7204 (1993)



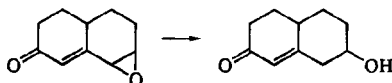
See page 229, Section 4.



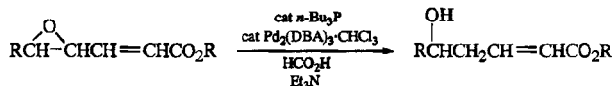
LiAlH_4	JACS 74 5917 (1952); 81 1643 (1959); 86 2657 (1964); 107 7978 (1985) JOC 33 423 (1968); 50 5910 (1985); 52 4898 (1987)
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HCO_2H , Et_3N , cat $n\text{-Bu}_3\text{P}$, cat $\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3$ CL 1775 (1986)
JACS 111 6280 (1989); 117 5958 (1995)

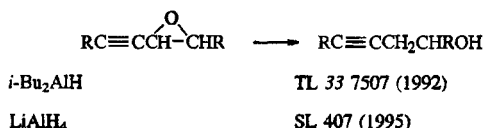
$(\text{NH}_4)_2\text{O}_2\text{CH}$, cat $n\text{-Bu}_3\text{P}$, cat $\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3$ CL 1017 (1984)



HCO_2H , Et_3N , cat $\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3$ TL 31 4757 (1990)
cat Pd-BaSO_4 , cyclohexene Helv 54 2775, 2785 (1971)
 $\text{Al}(\text{Hg})$, H_2O , HCl Steroids 27 603 (1976)



TL 32 4937 (1991)
JOC 58 2523 (1993)

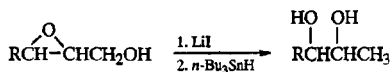


TL 33 7507 (1992)

SL 407 (1995)



JOC 50 5687 (1985)



JOC 60 4803 (1995)



NaBH_3CN , $\text{BF}_3 \cdot \text{OEt}_2$ TL 28 4569 (1987); 34 6285 (1993)

LiAlH_4 JOC 47 1378 (1982)

TL 28 2629 (1987)

$\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$ TL 23 2719, 4541 (1982); 27 3535 (1986); 28 703 (1987); 34 7425 (1993); 36 5967 (1995)
JOC 47 1378 (1982); 53 4081 (1988); 54 2817 (1989); 60 4264, 7230 (1995)
JACS 104 1109, 5521 (1982); 109 2205 (1987)
CC 1292 (1982); 1408 (1986); 311 (1987)
CL 175 (1983)

Cp_2TiCl , 1,4-cyclohexadiene JACS 116 986 (1994)

K, NH₃ (R = aryl)

JOC 57 965 (1992)

LiBH₄

TL 31 7467 (1990)

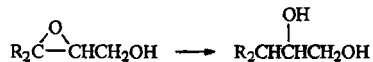
LiBH₄, Ti(O-*i*-Pr)₄

TL 27 4343 (1986); 31 7467 (1990)

i-Bu₂AlH

TL 23 2719, 3597 (1982); 32 5717 (1991); 34 7425 (1993)

JOC 59 3734 (1994)

LiBH₄, BH₃·THF

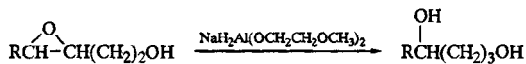
JOC 56 454 (1991)

NaBH₃CN, BF₃·OEt₂

JOC 59 4004 (1994)



JOC 57 5851 (1992)



TL 31 4301 (1990)

ReagentR'LiBH₄SiMe₃, Me, THP

TL 31 7467 (1990)

i-Bu₂AlHPhCH₂

TL 35 4409 (1994)

Ts

TL 35 7197 (1994)

LiI / *n*-Bu₃SnH

Ts

JOC 60 4803 (1995)

MgI₂ / *n*-Bu₃SnH

Ts

JOC 60 4803 (1995)

XReagent(s)

OTs

i-Bu₂AlH

TL 33 33 (1991)

MgI₂ / *n*-Bu₃SnH

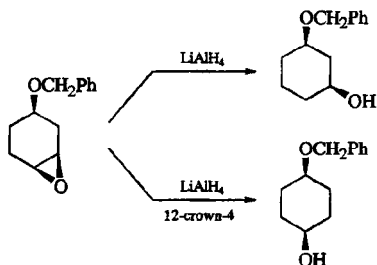
JOC 60 4803 (1995)

OMs

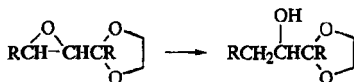
i-Bu₂AlH

TL 33 33 (1991)

Cl

LiAlH₄
LiHBEt₃TL 33 33 (1991)
TL 33 33 (1991)

JOC 55 4265 (1990); 57 1713 (1992); 59 4131 (1994)

LiAlH₄

JOC 50 5696 (1985)

TL 28 551 (1987); 33 8131 (1992)

Zn, Me₃SiCl

TL 28 551 (1987)

*n*-Bu₃SnH

JOC 57 5352 (1992)

PhSeNa, HOAc, EtOH

TL 28 4293 (1987)

N-acetylcysteine, borax, cat (PhSe)₂

JOC 59 5179 (1994)

Na[PhSeB(OEt)₃], EtOH

TL 29 347 (1988); 30 1819 (1989)

JACS 111 3728 (1989)

NaTeH

CL 271 (1984)

NaI, NaOAc, HOAc

TL 4377 (1974)

Na, NH₃, *t*-BuOH

JOC 60 833 (1995)

Ca, NH₃

JACS 111 2302 (1989); 115 3056 (1993)

Al(Hg)

CC 254 (1973)

JOC 38 3187 (1973); 43 3942 (1978); 52

3560 (1987)

Helv 57 781 (1974)

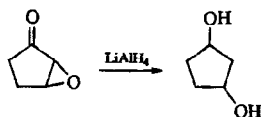
JACS 100 4618 (1978)

Steroids 34 683 (1979)

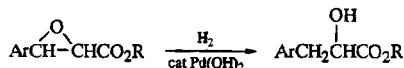
Al(Hg), NaHCO₃, ultrasound

TL 34 353 (1993)

CrCl_2	JOC 19 131 (1954)
$\text{Cr}(\text{OAc})_2$	JACS 77 4601 (1955) Helv 41 1667 (1958) Coll Czech Chem Commun 26 1207 (1961) JOC 37 565 (1972); 43 3946 (1978)
HCO_2H , Et_3N , cat $\text{Pd}(\text{OAc})_2$, cat dppe	CL 1975 (1989)
H_2 , cat Pd-C	CL 1975 (1989)
Zn, CH_3OH , HOAc	Chem Pharm Bull 24 2810 (1976)
SmI_2 , CH_3OH	JOC 51 2596 (1986)
electrolysis	JOC 46 5017 (1981); 55 1548 (1990)
$h\nu$, Et_3N	TL 32 1315 (1991); 36 7877 (1995)



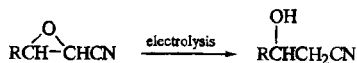
JOC 53 1623 (1988)



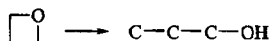
TL 35 5205 (1994)



H_2 , cat Pd-C	CL 1975 (1989)
NaTeH	CL 271 (1984)
K, biphenyl/ H_2O	Angew Int 25 653 (1986)
MgI_2 / n - Bu_3SnH	TL 28 4435 (1987)
SmI_2 , MeOH, THF	TL 32 4477 (1991)
SmI_2 , $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}$, THF, HMPA	TL 28 4437 (1987)
NaBH_4 , $(\text{PhSe})_2$, ROH, (HOAc)	CL 507 (1988) TL 31 3619, 4151 (1990) JACS 114 998 (1992)
electrolysis	JOC 55 1548 (1990)



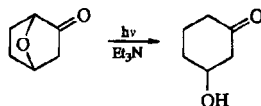
JOC 55 1548 (1990)

LiAlH₄

TL 79 (1969)
JOC 34 3579 (1969)
BCSJ 48 1907 (1975)

Raney Ni (2-aryl)

TL 79 (1969)
JOC 34 3579 (1969)



TL 32 1315 (1991)
JOC 60 8351 (1995)

 $n = 1, 2$ RLi(MgX) (R = *n*-Bu, *i*-Bu, *t*-Bu), MgBr₂

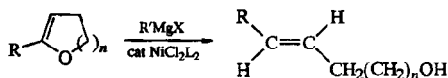
TL 32 4827 (1991)

i-Bu₂AlH

Angew Int 32 281 (1993)

i-Bu₂AlH, cat Ni(COD)₂

JACS 117 532 (1995)
TL 36 4185 (1995)

 $n = 1, 2$

JOC 49 4894 (1984); 58 1290 (1993)

3. Nucleophilic Opening of Cyclic Ethers

See also page 889, Section 2.

Review: Syn 225 (1994) ($n = 2$)

X	<i>n</i>	Reagent(s)
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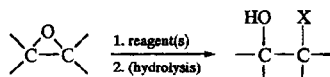
F	2	HF
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JACS 78 4956 (1956)
Org Rxs 21 125 (1974) (review)
TL 33 4145 (1992)

<u>X</u>	<u>n</u>	<u>Reagent(s)</u>	
F (<i>cont'd</i>)		HF-py	Israel J Chem 17 148 (1978) JOC 53 1026 (1988)
		HF-Et ₃ N	J Fluorine Chem 46 75 (1990)
		HF- <i>i</i> -Pr ₂ NH	BSCF 1890 (1965); 2850 (1966) JOC 53 1026 (1988)
		KHF ₂ , cat (<i>n</i> -Bu ₄ N)H ₂ F ₃ , phase transfer	TL 31 7209 (1990)
		SiF ₄ , <i>i</i> -Pr ₂ NEt	TL 29 4101 (1988); 30 967 (1989) JACS 115 8873 (1993)
		SiF ₄ , <i>n</i> -Bu ₄ NF, <i>i</i> -Pr ₂ NEt	TL 33 2319 (1992)
		[(Me ₂ N) ₃ S]Me ₃ SiF ₂ SbF ₃ , TiF ₄	TL 30 3557 (1989) SL 204 (1992)
Cl	2	HCl	Ber 49 477, 2778, 2782 (1916) JACS 63 2541 (1941); 76 1235, 1259 (1954) JCS 915 (1963); 644 (1965) JOC 55 4265 (1990); 57 1405, 1713, 5140 (1992); 58 6915 (1993); 59 4131 (1994) TL 33 585 (1992)
		NH ₄ Cl, LiClO ₄	JOC 59 4131 (1994)
		(Et ₃ NH)Cl	TL 30 1517 (1989)
		py·HCl	Syn Commun 11 287 (1981) JOC 54 4966 (1989)
		LiCl, HOAc	TL 32 3021 (1991); 33 585 (1992) JOC 58 6807 (1993)
		LiCl, Amberlyst	Syn Commun 22 1863 (1992)
		LiCl, TiCl ₄	SL 204 (1992)
		NaCl	JCS 915 (1963); 644 (1965)
		CIBH ₂ ·SMe ₂	TL 32 3719 (1991)
		BCl ₃ , (PhCH ₂ NEt ₃)Cl	TL 32 4623 (1991)
		(<i>lpc</i>) ₂ BCl (chiral)	JACS 110 6246 (1988)
		AlCl ₃	Tetr 25 1807 (1969) BCSJ 49 1063 (1976) JOC 57 5140 (1992)
		<i>i</i> -BuAlCl ₂	JOC 57 5140 (1992)
		Et ₂ AlCl	TL 33 4349 (1992)
		<i>i</i> -Bu ₂ AlCl	JOC 57 5140 (1992)
		Me ₃ SiCl (forms silyl ether)	TL 29 3307 (1988) JOC 57 3409 (1992)
		R ₃ SiCl, cat PPh ₃ (forms silyl ether)	TL 22 3803 (1981)
		R ₃ SiCl, cat <i>n</i> -Bu ₄ NCl (forms silyl ether)	TL 22 3803 (1981)
		SnCl ₄	JACS 76 1235 (1954)
		TiCl ₄	JOC 55 4265 (1990); 56 3988 (1991); 57 5140 (1992)
		TiCl ₄ , <i>t</i> -BuO ₂ H	JOC 57 1405, 1713 (1992)
		VCl ₃ (THF) ₃	SL 510 (1992)

		FeCl ₃	JOC 42 343 (1977)
		Li ₂ CuCl ₄	TL 27 3697 (1986); 36 8231 (1995)
		Cl ₂ , PPh ₃	TL 24 1307 (1983); 26 2011 (1985); 32 1307 (1983)
Br	2	HBr, NH ₄ Br or NaBr	JACS 76 1259 (1954)
		LiBr	JOC 55 5467 (1990); 59 7944 (1994)
		LiBr, Amberlyst	TL 32 3047 (1991)
		LiBr, HOAc	Syn Commun 22 1863 (1992)
		LiBr, TiCl ₄ or TiBr ₄	TL 32 3021 (1991)
		KBr, HOAc	SL 204 (1992)
		(Et ₂ NH ₂)Br, Ti(O- <i>i</i> -Pr) ₄	SL 897 (1993)
		TMPMgBr	TL 33 4349 (1992)
		(Ipc) ₂ BBr (chiral)	JOC 57 5140 (1992)
		(Me ₂ N) ₂ BBr	JACS 110 6246 (1988)
		AlBr ₃	TL 27 827 (1986)
		Me ₃ SiBr, Et ₃ N (forms silyl ether)	JOC 57 5140 (1992)
		Me ₃ SiBr, cat PPh ₃ (forms silyl ether)	Nouv J Chim 3 705 (1979)
		TiBr ₄	TL 22 3803 (1981)
		TiBr ₄ , Ti(NEt ₂) ₄	JOC 57 5140 (1992)
		Li ₂ NiBr ₄	JOC 57 5140 (1992)
		Li ₂ CuBr ₄	TL 25 2061 (1984)
		Br ₂	JOC 58 771 (1993)
		Br ₂ , PPh ₃	SL 248 (1991)
			TL 33 7093 (1992)
			TL 24 1307 (1983); 26 2011 (1985); 32 1307 (1983)
	2, 3	MgBr ₂	JACS 73 124 (1951); 76 1259 (1954)
			TL 29 5197 (1988); 32 3047 (1991)
			JOC 53 1184 (1988)
	2-4	Me ₂ BBr	TL 24 2969 (1983)
			JOC 52 1680 (1987); 59 1166 (1994)
		Me ₃ SiBr (forms silyl ether)	Ber 95 174 (1962)
			TL 4483 (1978); 29 3307 (1988)
			Syn 383 (1981)
			JOC 57 3409 (1992)
	2, 4-6	BBr ₃	Heterocycles 18 163 (1982)
	4	R ₄ NBr (R = Et, <i>n</i> -Bu)	JOC 51 3372 (1986)
I	2	HI	JACS 76 1259 (1954)
		LiI, Amberlyst	Syn Commun 22 1863 (1992)
		LiI, HOAc	TL 32 3021 (1991)
		LiI, BF ₃ ·OEt ₂	JACS 116 11287 (1994)
		LiI, TiCl ₄	JOC 57 5818 (1992)
		NaI, HOAc, NaOAc	SL 204 (1992)
		NaI, <i>p</i> -TsOH	TL 30 1583 (1989)
		MgI ₂	SL 384 (1990)
		(Ipc) ₂ BI (chiral)	TL 28 4435 (1987)
		AlI ₃	JACS 110 6246 (1988)
			TL 29 5815 (1988)
			JOC 57 5140 (1992)

<u>X</u>	<u>n</u>	<u>Reagent(s)</u>	
I (cont'd)		Me ₃ SiCl, NaI, H ₂ O	TL 35 745 (1994)
		Me ₃ SiI, cat PPh ₃ (forms silyl ether)	TL 22 3803 (1981)
		<i>t</i> -BuMe ₂ SiCl, NaI (forms silyl ether)	JOC 57 4110 (1992)
		Me ₃ SiI, Et ₃ N (forms silyl ether)	Nouv J Chim 3 705 (1979)
		I ₂ , acetone	TL 33 7093 (1992)
		I ₂ , PPh ₃	TL 24 1307 (1983); 26 2011 (1985); 32 1307 (1983)
	2, 4	<i>n</i> -Bu ₄ NI, BF ₃ ·OEt ₂	Syn 274 (1985)
		Me ₃ SiCl, NaI (forms silyl ether)	JOC 57 3365 (1992); 60 169 (1995)
		Me ₃ SiI (forms silyl ether)	Ber 95 174 (1962)
			TL 4483 (1978)
4			JOC 57 3409 (1992)
		NaI, AlCl ₃	TL 25 219 (1984)






Reviews:



Chem Rev 59 737 (1959)
 Angew Int 31 1179 (1992)

<u>X</u>	<u>Reagent(s)</u>	
OH	H ₂ O, Δ	JOC 48 1360 (1983)
	H ₂ O, pressure	TL 34 4031 (1993)
	H ₂ O, cat H ⁺	TL 3421 (1965)
		SL 507 (1994)
		JOC 59 1638 (1994); 60 41, 5224 (1995)
	H ₂ O, Nalfion-H	Syn 280 (1981)
	H ₂ O, Al ₂ O ₃	JOC 58 385 (1993)
	H ₂ O, cat NaO ₂ CPh	JOC 58 2331 (1993)
		SL 899 (1994)
	H ₂ O, cat KOH	TL 3421 (1965)
		JOC 59 1638 (1994)
	Me ₄ NOH	Austral J Chem 39 441 (1986)
	<i>t</i> -BuO ₂ H, TiCl ₄	JOC 57 1405 (1992)
	O ₂ , cat bis(3-methyl-2,4-pentanedionato)nickel(II)	CL 231 (1992)
	rabbit liver microsomal epoxide hydrolase (enantioselective)	JOC 45 299 (1980); 46 5148 (1981); 47 3105 (1982); 50 1471 (1985); 52 2886 (1987); 54 5978 (1989)
		JCS Perkin I 2717 (1983); 2715 (1988)
		TL 35 4219 (1994)
	<i>Aspergillus niger</i> (enantioselective)	JOC 58 5528 (1993)
	<i>Beauveria sulfurescens</i> (enantioselective)	JOC 58 5533 (1993)
	<i>Corynosporium cassiicola</i> (enantioselective)	TL 35 331 (1994)


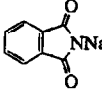
OR	ROH, cat H ₂ SO ₄	JACS 78 3851 (1956); 108 3040 (1986) JOC 55 4265 (1990); 57 1405, 1713 (1992); 60 41 (1995) SL 673 (1992)
	ROH, Nalfion-H	Syn 280 (1981)
	ROH, CF ₃ SO ₃ H	JOC 59 2945 (1994)
	ROH, 10-camphorsulphonic acid	JOC 57 5861 (1992)
	ROH, HBF ₄	SL 393 (1990)
	ROH, cat HClO ₄	JOC 55 1144 (1990)
	ROH, LiClO ₄	JOC 55 4265 (1990); 57 1405, 1713 (1992) SL 673 (1992)
	ROH, NaClO ₄	JOC 57 1405 (1992) SL 673 (1992)
	ROH, KClO ₄	JOC 57 1405 (1992)
	ROH, Mg(ClO ₄) ₂	JOC 57 1405 (1992) SL 673 (1992)
	ROH, CaCl ₂	SL 673 (1992)
	ROH, cat BF ₃ ·OEt ₂	TL 29 4393 (1988); 34 4297 (1993) JOC 54 4637, 4643 (1989); 59 537, 3135 (1994)
	ROH, SnCl ₄	TL 33 2191 (1992)
	ROH, organotin phosphate condensates	Organomet 3 426 (1984) TL 26 3219 (1985)
		JOC 53 275 (1988) SL 97 (1991)
	ROH, ZnCl ₂	TL 32 4035 (1991)
	ROH, Zn(OTf) ₂	JOC 57 1405 (1992) SL 673 (1992)
	ROH, DDQ	TL 31 735 (1990) JOC 58 7929 (1993)
	ROH, cat TCNE	SL 847 (1993)
	ROH, Na	TL 34 5847 (1993)
	ROH, Al ₂ O ₃	TL 3597 (1975) JACS 99 8208 (1977) Angew Int 17 487 (1978) (review)
	NaOCH ₃ , CH ₃ OH	JOC 52 4812 (1987); 58 385 (1993)
	NaOCH ₃ , THF	JOC 53 1084 (1988)
	NaOR	JACS 78 3851 (1956) SL 673 (1992) JOC 59 1907 (1994)
	NaOCH ₂ Ph	SL 225 (1991); 491 (1994)
	KOCH ₂ Ph	JOC 54 3354 (1989)
	For intramolecular reactions, see page 889, Section 2.	
OAr	ArOH, NaH	TL 34 7483 (1993)
	ArOH, cat Et ₃ N	TL 36 2379 (1995)
	ArOH, [MeP(OPh) ₃]I	TL 31 6325 (1990) (intramolecular)
	ArOH, SnCl ₄	TL 31 6325 (1990) (intramolecular)
	ArOSiMe ₃ , cat CsF	TL 31 1723 (1990)
O ₂ CH	(NH ₄)O ₂ CH. HCO ₂ H	JOC 54 2781 (1989)

<u>X</u>	<u>Reagent(s)</u>	
O ₂ CR	RCO ₂ H, NaO ₂ CR	JOC 59 1283 (1994)
	RCO ₂ H, Al ₂ O ₃	TL 3597 (1975) JACS 99 8208 (1977); 111 636 (1989) Angew Int 17 487 (1978) (review) Syn Commun 11 737 (1981) JOC 58 385 (1993) TL 35 4727 (1994) SL 783 (1991) JACS 110 6192 (1988)
O ₃ SCF ₃	RCO ₂ H, AlMe ₃	TL 35 4727 (1994)
	RCO ₂ H, cat FeCl ₃	SL 783 (1991)
	NH ₄ (O ₂ CR), Ti(O- <i>i</i> -Pr) ₄	JACS 110 6192 (1988)
O ₃ SCF ₃	Me ₃ SiO ₃ SCF ₃	JACS 101 2738 (1979)
SH	Ph ₃ SiSH, Et ₃ N, MeOH	TL 34 3363 (1993)
SR	RSH, LiClO ₄	SL 303 (1992)
	RSH, Mg(ClO ₄) ₂	SL 303 (1992)
	RSH, Al ₂ O ₃	TL 3597 (1975) JACS 99 8208 (1977) Angew Int 17 487 (1978) (review) SL 25 (1993) BCSJ 62 597 (1989) JOC 55 2536 (1990) BCSJ 61 1213 (1988) SL 167 (1995) CL 1643 (1985) BCSJ 61 1213 (1988) TL 28 6065 (1987) SL 303 (1992); 167 (1995) TL 34 7187 (1993) JOC 60 7778 (1995) JOC 57 4215 (1992) JOC 53 1084 (1988); 58 6114 (1993) SL 427 (1995) TL 21 1485 (1980) JOC 57 3409 (1992) Angew Int 25 653 (1986)
	PhSH, SiO ₂	SL 25 (1993)
	PhSH, cat <i>n</i> -Bu ₄ NBr	BCSJ 62 597 (1989)
	RSH, cat Mn tartrate (enantioselective)	JOC 55 2536 (1990)
	PhSH, ZnCl ₂	BCSJ 61 1213 (1988)
	RSH, cat Zn tartrate (enantioselective)	SL 167 (1995)
	RSH; cat SmCl ₃ , CeCl ₃ or Eu(fod) ₃	CL 1643 (1985)
	RSH, Et ₃ N	BCSJ 61 1213 (1988)
	PhSH, NaOH	TL 28 6065 (1987)
	RSH, NaOMe	SL 303 (1992); 167 (1995)
	NaSR	TL 34 7187 (1993)
	Me ₃ SiSR	JOC 60 7778 (1995)
	Me ₃ SiSR, <i>n</i> -BuLi or ZnCl ₂	JOC 57 4215 (1992)
	Li, K or Mg; naphthalene or biphenyl/ RSSR	JOC 53 1084 (1988); 58 6114 (1993)
	PhSSPh, NaBH ₄ -Amberlite IRA-400, MeOH	SL 427 (1995)
-S-	0.5 Ph ₃ SiSH, CsCO ₃ , MeOH	TL 21 1485 (1980)
SePh	PhSeH, Al ₂ O ₃	JOC 57 3409 (1992)
	(K)NaSePh	Angew Int 25 653 (1986)
		JOC 59 3490 (1994)
		JACS 99 8208 (1977)
		Angew Int 17 487 (1978) (review) JACS 95 2697 (1973); 99 8208 (1977); 106 7854 (1984); 107 1691, 1777 (1985) TL 5087 (1978) Tetr 34 1049 (1978) JOC 51 2148 (1986) JOC 50 5897 (1985) CL 909 (1979)
	<i>i</i> -Bu ₂ AlSePh	
	Me ₃ SiSePh, cat ZnI ₂ or <i>n</i> -BuLi	

NH ₂	NH ₃	JACS 95 6853 (1973) JOC 58 4756 (1993); 59 1755 (1994); 60 6129 (1995) JOC 60 41 (1995)
	KN(SiMe ₃) ₂ /HCl	
NHR	RNH ₂	BCSJ 40 2401 (1967) Chem Pharm Bull 26 394 (1978) JOC 50 3948 (1985) (intramolecular); 56 95 (1991); 59 1907, 4381 (intramolecular) (1994); 60 5958, 6688 (1995) TL 26 4617 (1985) (intramolecular); 28 1603 (1987); 30 5721 (1989) (intramolecular); 33 7413 (1992); 35 3293 (1994); 36 8247 (1995) (intramolecular) JACS 112 9364 (1990); 116 8544 (1994) TL 33 4077 (1992)
	RNH ₂ , rat liver microsomes (enantioselective)	
	RNH ₂ , zeolite	CL 779 (1985)
	RNH ₂ , EtOH	JOC 56 7043 (1991)
	RNH ₂ , Al ₂ O ₃	TL 30 5425 (1989)
	RNH ₂ , cat Ph ₄ SbOTf	TL 30 739 (1989)
	ArNH ₂ , cat Mn tartrate (enantioselective)	BCSJ 61 1213 (1988)
	ArNH ₂ , cat CoCl ₂	TL 31 575 (1990)
	RNH ₂ / <i>n</i> -BuLi/Me ₃ Al	TL 33 5351 (1992) (intramolecular)
	LiAl(NHR) ₄	JOC 57 5831 (1992); 60 3494 (1995)
	Me ₃ SiNHR	TL 27 2451 (1986) (aryl epoxides only)
	Me ₃ SiNHR, cat Cr(NBu ^t) ₂ Cl ₂	TL 36 107 (1995)
	RN ₃ , H ₂ , reducing agent	See page 815, Section 6.
NHR, NR ₂	RNH ₂ or R ₂ NH	TL 31 7579 (1990); 34 4403 (1993); 35 9375 (1994); 36 6599 (1995)
	RNH ₂ or R ₂ NH, LiClO ₄	TL 31 4661 (1990); 35 433 (1994) JOC 56 5939 (1991)
	RNH ₂ or R ₂ NH; NaClO ₄ , Mg(ClO ₄) ₂ , LiBF ₄ , CaCl ₂ or Zn(OTf) ₂	TL 31 4661 (1990)
	RNH ₂ or R ₂ NH, cat M(OTf) ₃ (M = Yb, Nd, Gd)	TL 35 433 (1994)
	RNH ₂ or R ₂ NH, cat SmI ₂	TL 36 1649 (1995)
	RNH ₂ or R ₂ NH, zeolite	CL 779 (1985)
	LiNHR or LiNR ₂	JOC 59 7746 (1994)
	LiNHR or LiNR ₂ , cat RNHB  or R ₂ NB 	JOC 59 7746 (1994)
	LiNHR or LiNR ₂ , cat BrB 	JOC 59 7746 (1994)
	(RNH) ₂ Cu(CN)Li ₂ or (R ₂ N) ₂ Cu(CN)Li ₂	CC 1201 (1993)
NR ₂	R ₂ NH	JOC 58 4043, 6804 (1993); 59 4131 (1994); 60 41 (1995)
	R ₂ NH, H ₂ O	JOC 56 3133 (1991)

<u>X</u>	<u>Reagent(s)</u>	
NR ₂ (continued)	R ₂ NH, EtOH	JOC 56 5939, 7043 (1991)
	R ₂ NH, LiClO ₄	JOC 56 7043 (1991); 59 4131 (1994)
	R ₂ NH, NaClO ₄	JOC 56 5939 (1991)
	R ₂ NH, Mg(ClO ₄) ₂	JOC 56 5939 (1991)
	R ₂ NH, CaCl ₂	JOC 56 5939 (1991)
	R ₂ NH, Al ₂ O ₃	JACS 99 8208 (1977)
		Angew Int 17 487 (1978) (review)
		TL 34 7035 (1993)
	R ₂ NH, EtAlCl ₂ -BINOL (enantioselective)	SL 69 (1994)
	R ₂ NH, Et ₂ AlCl-BINOL (enantioselective)	SL 893 (1993); 69 (1994)
	R ₂ NH, Et ₃ Al-BINOL (enantioselective)	SL 893 (1993); 69 (1994)
	R ₂ NH, SiO ₂	TL 31 7591 (1990)
		SL 703 (1993)
	R ₂ NH, Ti(O- <i>i</i> -Pr) ₄ -BINOL (enantioselective)	SL 893 (1993); 69 (1994)
	R ₂ NH, Zn(OTf) ₂	JOC 56 5939 (1991)
	R ₂ NH, cat Ph ₄ SbOTf	TL 30 739 (1989)
	R ₂ NMgX	JOC 56 7043 (1991)
	Et ₂ AlNR ₂	TL 22 195 (1981)
	Me ₃ SiNR ₂	JOC 32 2210 (1967)
	Me ₃ SnNR ₂	JOC 56 7043 (1991)
	<i>n</i> -Bu ₃ SnNR ₂ , cat LiNR ₂	JOMC 8 255 (1967)
	<i>n</i> -Bu ₃ PbNR ₂	TL 30 4255 (1989)
		TL 30 1517 (1989)
N ₃	HN ₃ , Et ₃ Al	Helv 69 415 (1986)
	LiN ₃	TL 31 5641 (1990)
		JOC 56 7043 (1991)
		SL 403 (1991)
		Syn 821 (1992)
	LiN ₃ , NH ₄ Cl	JOC 57 5692 (1992)
	NaN ₃	JACS 74 1168 (1952)
		JOC 43 4271 (1978); 53 1184 (1988);
		54 4525 (1989); 55 1957 (1990); 56
		3849, 7043 (1991); 60 41, 790
		(1995)
		TL 31 5641 (1990); 36 6599 (1995)
	NaN ₃ , NH ₄ Cl	JOC 32 511 (1967); 55 1749 (1990);
N ₃		56 7043 (1991); 57 1713 (1992);
		58 6090 (1993); 59 813, 4131, 4450,
		4800, 4875, 7944, 7962 (1994); 60
		6103 (1995)
		TL 31 279, 1335, 5641 (1990); 34
		5491 (1993); 35 359, 887 (1994); 36
		3639 (1995)
		Tetr Asym 5 1727 (1994)
		JACS 116 487 (1994); 117 2128
		(1995)

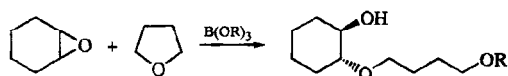
- NaN_3 , H_2SO_4 JOC 43 4271 (1978); 54 4525 (1989);
 56 7043 (1991)
 TL 31 5641 (1990)
- NaN_3 , LiOTf TL 31 5641 (1990)
- NaN_3 , LiClO_4 TL 31 5641 (1990); 36 6887 (1995)
 JOC 56 7043 (1991); 57 1713 (1992);
 59 4131 (1994)
- NaN_3 , NaClO_4 JOC 56 7043 (1991)
- NaN_3 , $\text{Mg}(\text{ClO}_4)_2$ TL 31 5641 (1990)
 JOC 56 7043 (1991)
- NaN_3 , SiO_2 TL 36 6887 (1995)
- NaN_3 , $\text{Zn}(\text{OTf})_2$ TL 31 5641 (1990)
 JOC 56 7043 (1991)
- NaN_3 , *Rhodococcus* sp. (enantioselective) TL 35 81 (1994)
- $(n\text{-Bu}_4\text{N})\text{N}_3$ SL 167 (1995)
- Me_3SiN_3 Ann 266 (1975)
 TL 30 4153 (1989); 33 7413 (1992)
 SL 403 (1991)
- Me_3SiN_3 , $\text{BF}_3 \cdot \text{OEt}_2$ Ann 165 (1987)
- Me_3SiN_3 , cat $\text{Al}(\text{O-}i\text{-Pr})_3$ Syn 541 (1988)
 TL 30 4673 (1989)
 JOC 56 7043 (1991)
- Me_3SiN_3 , cat Ph_4SbOH Tetr 47 1435 (1991)
- Me_3SiN_3 , cat $\text{Ti}(\text{O-}i\text{-Pr})_4$ JACS 117 4729 (1995)
 TL 36 4849 (1995)
- Me_3SiN_3 , cat $\text{Ti}(\text{O-}i\text{-Pr})_4$ TL 24 4189 (1983); 27 4423 (1986); 30
 4673 (1989)
 J Mol Catal 34 39 (1986)
- Me_3SiN_3 , cat $\text{Ti}(\text{O-}i\text{-Pr})_4$, cat chiral diols
 or amino alcohols (enantioselective) Tetr 47 1435 (1991)
- Me_3SiN_3 , cat $\text{TiCl}_2(\text{O-}i\text{-Pr})_2$ -dialkyl
 tartrate (enantioselective) JOC 56 7043 (1991); 57 3409 (1992)
- R_3SiN_3 , cat chiral Zr alkoxide, cat
 Me_3SiOTf (enantioselective) JOMC 346 C7 (1988)
- Me_3SiN_3 , cat $\text{VO}(\text{O-}i\text{-Pr})_3$ SL 774 (1991)
- Me_3SiN_3 , cat Cp_2VCl_2 JACS 114 2768 (1992)
- Me_3SiN_3 , cat Cr salen (enantioselective) TL 24 4189 (1983)
- Me_3SiN_3 , cat $\text{Cr}(\text{NBu}^t)_2\text{Cl}_2$ J Mol Catal 34 39 (1986)
- Me_3SiN_3 , cat Mn, Cu or Zn tartrate
 (enantioselective) TL 24 4189 (1983)
- Me_3SiN_3 , cat $\text{W}(\text{NBu}^t)_2(\text{NHBu}^t)_2$ JACS 117 5897 (1995)
- Me_3SiN_3 , cat ZnCl_2 TL 36 107 (1995)
- Me_3SiN_3 , cat Sml_2 BCSJ 61 1213 (1988)
- Me_3SiN_3 , cat $\text{Sml}_2(\text{O-}i\text{-Bu})$ TL 36 107 (1995)
- Me_3SiN_3 , CsF or $n\text{-Bu}_4\text{NF}$ JOC 55 1169 (1990)
- Me_3SnN_3 TL 36 1649 (1995)
- $n\text{-Bu}_3\text{SnN}_3$ TL 36 1649 (1995)
- $n\text{-Bu}_3\text{SnN}_3$ SL 403 (1991)
- $n\text{-Bu}_3\text{SnN}_3$ SL 403 (1991)
- $n\text{-Bu}_3\text{SnN}_3$ TL 30 4153 (1989)
- $n\text{-Bu}_3\text{SnN}_3$ JOC 56 7043 (1991)
- $n\text{-Bu}_3\text{SnN}_3$ SL 403 (1991); 999 (1992)

<u>X</u>	<u>Reagent(s)</u>	
N_3 (continued)	$n\text{-Bu}_2\text{Sn}(N_3)_2$ $Ti(O\text{-}i\text{-Pr})_2(N_3)_2$ $VO(O\text{-}i\text{-Pr})(N_3)_2$ tetramethylguanidinium azide Amberlite azide	TL 31 221 (1990) J Mol Catal 34 39 (1986) JOC 56 7043 (1991) J Mol Catal 34 39 (1986) TL 36 6887 (1995) JOC 55 4892 (1990)
NRCOR	$Me_3SiNRCOR$, cat $NaOSiMe_3$	Ber 102 14 (1969)
NRTs	HNRTs, NaOH	Tetr 47 3075 (1991) TL 33 487 (1992); 34 2315 (1993) (all intramolecular)
		TL 36 6599 (1995)
$\text{—N}\equiv\text{C}$	Me_3SiCN ; cat $Pd(CN)_2$, $SnCl_2$ or Me_3Ga (forms silyl ether) Me_3SiCN , cat $ZnCl_2$ (forms silyl ether) Me_3SiCN , cat ZnI_2 (forms silyl ether)	JOC 52 1013 (1987) TL 24 655 (1983) JACS 104 5849 (1982) TL 25 3259 (1984); 27 6307 (1986) Org Syn 64 39 (1986) JOC 51 5010 (1986) Org Syn Coll Vol 7 294 (1990)
PPh_3	PPh_3 , PhOH	SL 269 (1994)
$PO(OR)_2$	$NaOP(OR)_2$, $BF_3\cdot OEt_2$	JOC 58 5779 (1993)
$\text{—C}\equiv\text{N}$	LiCN NaCN KCN KCN, HOAc KCN, NH_4Cl KCN, $LiClO_4$ KCN, $Mg(ClO_4)_2$ KCN, $n\text{-Bu}_4NI$, $Ti(O\text{-}i\text{-Pr})_4$ ($n\text{-Bu}_4N$)CN HCN, Et_3Al Et_2AlCN Me_3SiCN , cat KCN, cat 18-crown-6 (forms silyl ether) Me_3SiCN , CaO or MgO (forms silyl ether) Me_3SiCN ; $Al(O\text{-}i\text{-Pr})_3$, $i\text{-Bu}_2AlO\text{-}i\text{-Pr}$ or Et_2AlCl (forms silyl ether) Me_3SiCN , cat $AlCl_3$ (forms silyl ether) Me_3SiCN , cat Et_2AlCl (forms silyl ether) Me_3SiCN , Me_3Al (forms silyl ether)	TL 33 1431 (1992) JACS 106 462 (1984) JOC 60 41 (1994) JOC 57 4441 (1992) JOC 53 5590 (1988) TL 32 4775 (1991) TL 32 4775 (1991); 34 5127 (1993) SL 853 (1994) TL 32 4775 (1991) JOC 53 1184 (1988) SL 167 (1995) JCS C 2365 (1970) JCS C 2365 (1970) JOC 59 4297 (1994) JOC 55 2016 (1990) CL 481 (1990) JOC 52 1013 (1987) TL 1449 (1973) JOC 47 2873 (1982) JOC 57 3409 (1992)

Me_3SiCN , cat $\text{Ti}(\text{O}-i\text{-Pr})_4$ (forms silyl ether)	JOC 50 1557 (1985)
Me_3SiCN , cat $\text{Ti}(\text{O}-i\text{-Pr})_4$, cat Schiff base (forms silyl ether)	J Mol Catal 49 L23 (1988) SL 663 (1992)
Me_3SiCN , cat $\text{Yb}(\text{CN})_3$ (forms silyl ether)	TL 31 6209 (1990)
Me_3SiCN , cat MCl_3 ($\text{M} = \text{Sm}, \text{La}, \text{Ce}$) (forms silyl ether)	TL 28 5513 (1987)
Me_3SiCN , cat SmI_2 (forms silyl ether)	TL 36 1649 (1995)
$\text{Me}_2\text{C}(\text{OH})\text{CN}$, Et_3N	TL 33 3281 (1992)
$\text{Me}_2\text{C}(\text{OH})\text{CN}$, cat $\text{M}(\text{O}-i\text{-Pr})_3$ ($\text{M} = \text{Ce}, \text{La}, \text{Sm}, \text{Yb}$)	CL 975 (1993)

SiMe₃

$(\text{Me}_3\text{Si})_2$, cat KOMe, HMPA (forms silyl ether) JOC 57 4638 (1992)



R = Ph, Ac

SL 565 (1992)

XReagent(s)

Cl

 Li_2CuCl_4

SL 607 (1993)

Br

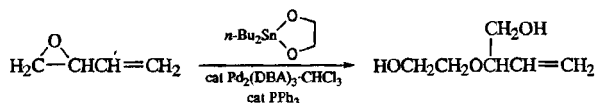
 Li_2NiBr_4

SL 607 (1993)

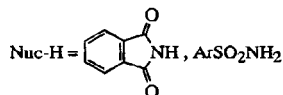
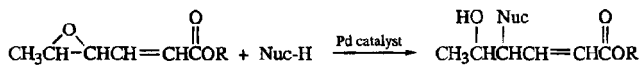
OR

ROH, $\text{BF}_3 \cdot \text{OEt}_2$

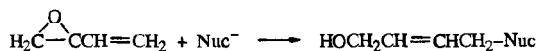
SL 899 (1994)



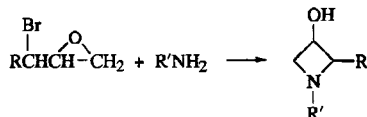
TL 29 2931 (1988)



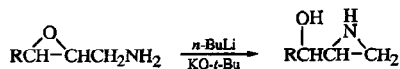
JOC 54 977 (1989)



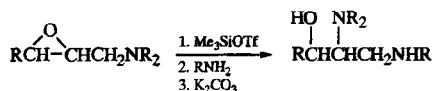
See page 234, Section 6.



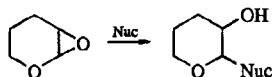
JOC 32 2972 (1967); 59 2172 (1994)



JOC 60 2044 (1995)



SL 1037 (1995)

Nuc $n\text{-Bu}_4\text{NF}$

Carbohydr Res 206 361 (1990)

JACS 114 4518 (1992)

 $\text{ROH}, \text{Cs}_2\text{CO}_3$

JOC 58 3761 (1993)

 $\text{ROH}, \text{ZnCl}_2$

JACS 111 6661 (1989); 114 4518 (1992)

Carbohydr Res 206 361 (1990)

 NaOR

JOC 58 3761 (1993)

 NaSPh

JOC 58 3761 (1993)

 $(n\text{-Bu}_4\text{N})\text{SPh}$

Carbohydr Res 206 361 (1990)

JACS 114 4518 (1992)

 PhSeH

Carbohydr Res 206 361 (1990)

 $\text{RNH}_2, \text{ZnCl}_2$

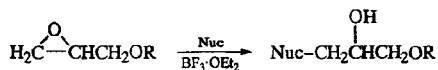
Carbohydr Res 206 361 (1990)

 NaN_3

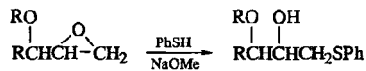
JOC 58 3761 (1993)

 $(n\text{-Bu}_4\text{N})\text{N}_3$

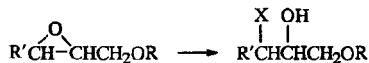
Carbohydr Res 206 361 (1990)

 $\text{R} = \text{ArSO}_2, \text{SiR}_3; \text{Nuc} = \text{ROH}, \text{PhSH}$

JACS 111 3077 (1989)



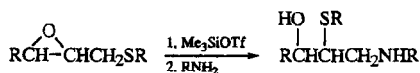
JOC 60 5048 (1995)



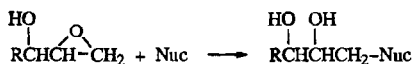
<u>X</u>	<u>Reagent(s)</u>	<u>R</u>	
F	(<i>n</i> -Bu ₄ N)H ₂ F ₃	PhCH ₂ , Ac, PhCO	TL 33 7083 (1992)
Cl	LiCl, Amberlyst	PhCH ₂ , R ₃ Si	Syn Commun 22 1863 (1992)
	LiCl, TiCl ₄	PhCH ₂ , Ac, MEM	JOC 60 4803 (1995)
	ClBH ₂ ·SMe ₂	PhCH ₂ , Ac, R ₃ Si	SL 204 (1992)
Br	LiBr, Amberlyst	PhCH ₂ , SiR ₃	TL 33 6181 (1992)
			Syn Commun 22 1863 (1992)
I	LiI, Amberlyst	PhCH ₂ , SiR ₃	JOC 60 4803 (1995)
			Syn Commun 22 1863 (1992)
	MgI ₂	PhCH ₂ , Ac, R ₃ Si	JOC 56 6206 (1991)
OMe	MeOH, H ₂ SO ₄	PhCH ₂	JOC 58 1221 (1993)
	MeOH, LiClO ₄	PhCH ₂	JOC 58 1221 (1993)
	MeOH, Mg(ClO ₄) ₄	PhCH ₂	JOC 58 1221 (1993)
	NaOMe	PhCH ₂	JOC 58 1221 (1993)
NR ₂	R ₂ NH	PhCH ₂	JOC 58 1221 (1993)
	R ₂ NH, LiClO ₄	PhCH ₂	JOC 58 1221 (1993)
N ₃	NaN ₃ , NH ₄ Cl	PhCH ₂	JOC 58 1221 (1993)
	NaN ₃ , LiClO ₄	PhCH ₂	JOC 58 1221 (1993)
	NaN ₃ , Mg(ClO ₄) ₂	PhCH ₂	JOC 58 1221 (1993)
	NaN ₃ , Zn(OTf) ₂	PhCH ₂	JOC 58 1221 (1993)



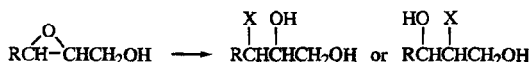
<u>X</u>	<u>Reagent(s)</u>	
Cl	Et ₂ AlCl	CL 1787 (1991)
Br	Et ₂ AlCl, (Et ₂ NH ₂)Br	CL 1787 (1991)
		IACS 115 9305 (1993)
Cl, Br, I	LiX, Amberlyst	TL 35 797 (1994)
I	MgI ₂	TL 35 797 (1994)
OH	H ₂ O, cat HClO ₄	JOC 50 5687 (1985)
OR	ROH, cat HClO ₄	JOC 50 5687 (1985)
	ROH, cat BF ₃ ·OEt ₂	SL 745 (1994)



TL 36 8327 (1995)



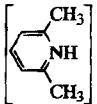
<u>X</u>	<u>Reagent(s)</u>	
I	I ₂ , Ti(O- <i>i</i> -Pr) ₄	JOC 55 3429 (1990)
SR	RSH, NaOH	JOC 50 5687 (1985)
N ₃	NaN ₃	JOC 50 5687 (1985)
CN	KCN	JOC 50 5687 (1985)



<u>X</u>	<u>Reagent(s)</u>	
SPh	NaSPh	JOC 50 5696 (1985)
SePh	NaSePh	JOC 50 5696 (1985)
N ₃	NaN ₃	JOC 50 5696 (1985)
	Ti(O- <i>i</i> -Pr) ₂ (N ₃) ₂	TL 30 7205 (1989)
CN	KCN, Ti(O- <i>i</i> -Pr) ₄ , <i>n</i> -Bu ₄ NI or 18-crown-6	JOC 50 1557 (1985)



<u>X</u>	<u>Reagents</u>	
F	<i>i</i> -Pr ₂ NH·(HF) ₃ (<i>n</i> -Bu ₄ N)H ₂ F ₃ (<i>i</i> -PrO) ₂ TiF ₂	CL 1689 (1989) TL 33 7083 (1992) TL 33 7083 (1992)
Cl	LiCl, TiCl ₄ LiCl, Amberlyst ClBH ₂ ·SMe ₂ NH ₄ Cl, Ti(O- <i>i</i> -Pr) ₄ Et ₃ NHCl, Ti(O- <i>i</i> -Pr) ₄ (<i>i</i> -PrO) ₃ TiCl (<i>i</i> -PrO) ₂ TiCl ₂ , diethyl tartrate	SL 204 (1992) Syn Commun 22 1863 (1992) JOC 60 4803 (1995) TL 33 6181 (1992) JOC 50 1557 (1985); 56 1347 (1991) JACS 110 2248 (1988) Tetr Asym 2 1083 (1991) TL 27 6031 (1986)
Br	NH ₄ Br LiBr, Amberlyst Br ₂ , Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985) Syn Commun 22 1863 (1992) JOC 60 4803 (1995) JOC 55 3429 (1990)

I	LiI, Amberlyst	Syn Commun 22 1863 (1992)
	MgI ₂	JOC 60 4803 (1995)
	I ₂ , Ti(O- <i>i</i> -Pr) ₄	JOC 56 6206 (1991) JOC 55 3429 (1990)
OMe	MeOH, H ₂ SO ₄	JOC 58 1221 (1993)
	MeOH, LiClO ₄	JOC 58 1221 (1993)
OR	ROH, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985)
	Ti(OR) ₄	JOC 60 5048 (1995)
OAr	NaOAr, Ti(O- <i>i</i> -Pr) ₄	JOC 51 3710 (1986); 51 5413 (1986)
	(<i>i</i> -PrO) ₃ TiOAr	TL 29 3671 (1988) Tetr Asym 2 1083 (1991)
O ₂ CR	RCO ₂ H, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985); 52 4973 (1987); 54 4268 (1989)
	(NH ₄)O ₂ CR, Ti(O- <i>i</i> -Pr) ₄	TL 27 4987, 4991 (1986); 29 2701 (1988)
	(<i>i</i> -PrO) ₃ TiO ₂ CR	JOC 50 1557 (1985)
		Tetr Asym 2 1083 (1991)
OTs	 OTs, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985)
SCOPh	(<i>i</i> -PrO) ₂ TiSCOPh	Tetr Asym 2 1083 (1991)
SPh	PhSH, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985); 51 5413 (1986)
	PhSH, PhSNa, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985)
SCN	NH ₄ SCN, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985)
SePh	PhSeH, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985)
NHR	RNH ₂ , Ti(O- <i>i</i> -Pr) ₄	TL 32 6931 (1991); 34 7781 (1993); 36 3019 (1995)
NR ₂	R ₂ NH	JOC 58 1221 (1993)
	R ₂ NH, LiClO ₄	JOC 58 1221 (1993)
	R ₂ NH, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985); 51 5413 (1986)
		TL 32 6931 (1991)
N ₃	NaN ₃ , NH ₄ Cl	JOC 50 1557 (1985); 54 1116 (1989); 58 1221 (1993)
	NaN ₃ , zeolite	CL 1327 (1986)
		JOC 54 1116 (1989)
	NaN ₃ , LiClO ₄	JOC 58 1221 (1993)
	Me ₃ SiN ₃ , Et ₂ AlF	CL 599 (1985)
		JOC 56 2614 (1991)
	Me ₃ SiN ₃ , Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985); 54 1116 (1989)
		JACS 113 5117 (1991)
CN	(<i>i</i> -PrO) ₂ Ti(N ₃) ₂	TL 36 811 (1995) JOC 53 5185 (1988)
	Me ₃ SiCN, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1557 (1985)

XReagent(s)

Br

 Li_2NiBr_4

JOC 56 815 (1991)

 NR_2 R_2AlNR_2

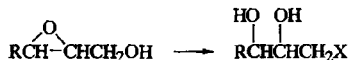
JOC 58 52 (1993)

 N_3 $\text{NaN}_3, \text{NH}_4\text{Cl}$

CL 599 (1985)

JOC 52 3337 (1987)

TL 32 679 (1991)

XReagent(s)

I

LiI

TL 33 7429 (1992)

JOC 60 4803 (1995)

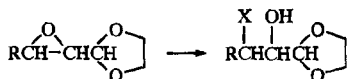
SR

 RSH, NaOH

JOC 50 5687 (1985)

 NR_2 R_2NH

JOC 50 5687 (1985)

XReagent

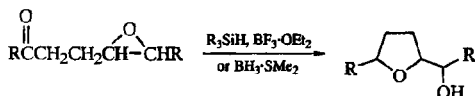
SPh

 NaSPh

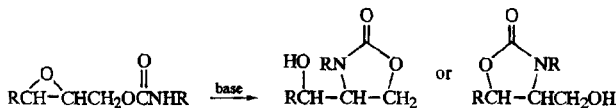
JOC 50 5696 (1985)

 N_3 NaN_3

JOC 50 5696 (1985)



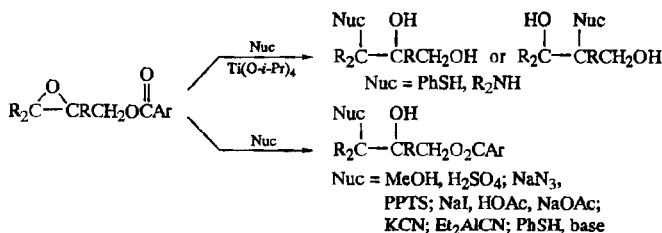
JOC 53 1082 (1988); 56 4141 (1991)



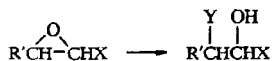
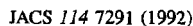
JOC 50 3752 (1985); 55 5700 (1990)

TL 29 5205 (1988); 35 4935 (1994)

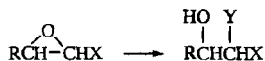
JACS 116 8544 (1994)



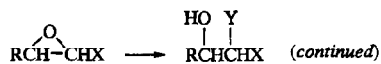
JOC 50 5696 (1985)



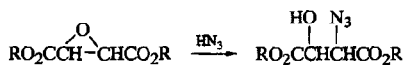
X	Y	Reagent(s)	
CO ₂ H	Cl	LiCl, TiCl ₄	SL 204 (1992)
	SR	RSH, cat NaOMe	JOC 58 6247 (1993)
	SPh	PhSH or PhSNa, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1560 (1985)
	NHAr	ArNH ₂	Arch Pharm 312 26 (1979)
	NR ₂	R ₂ NH	Arch Pharm 312 138 (1979)
		R ₂ NH, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1560 (1985)
CO ₂ R	F	(Me ₃ NH)HF ₂	BSCF 2721 (1969)
		py·(HF) _n	J Fluorine Chem 17 565 (1981)
		LiCl, TiCl ₄	SL 204 (1992)
		(Et ₂ NH ₂)Br, Et ₂ AlCl	JOC 58 1287 (1993)
	OR	ROH, AlPO ₄ -Al ₂ O ₃	CL 1565 (1986)
	OAr	ArOH, AlPO ₄ -Al ₂ O ₃	CL 1565 (1986)
	O ₂ CR	RCO ₂ H, AlPO ₄ -Al ₂ O ₃	CL 1565 (1986)
	SAr	ArSH	JOC 57 851 (1992)
		ArSH, AlPO ₄ -Al ₂ O ₃	CL 1565 (1986)
	NH ₂	NH ₃	Arch Pharm 307 871 (1974); 308 135 (1975)
			JCS Perkin I 1618 (1980)
			JOC 57 4320 (1992)
			TL 36 5417 (1995)
	NHR	PhCH ₂ NH ₂	Arch Pharm 312 26 (1979)
	NHAr	ArNH ₂	Arch Pharm 312 138 (1979)
	NR ₂	R ₂ NH	CL 1565 (1986)
	NHAc	MeCN, AlPO ₄ -Al ₂ O ₃	TL 30 4881 (1989)
	N ₃	NaN ₃ , NH ₄ Cl	JOC 58 1287, 1762 (1993)
	⁺ PPh ₃	PPh ₃ , PhOH	SL 269 (1994)
CONR ₂	F	py·(HF) _n	J Fluorine Chem 17 565 (1981)
	SPh	PhSH, Ti(O- <i>i</i> -Pr) ₄	JOC 50 1560 (1985)
	SR	NaSR, Ti(O- <i>i</i> -Pr) ₄	JOC 58 6247 (1993)
	NHAr	ArNH ₂	Arch Pharm 312 26 (1979)
	NR ₂	R ₂ NH	BCSJ 54 2136 (1981)
			Arch Pharm 312 138 (1979); 314 464 (1981)
	N ₃	NaN ₃ , MgSO ₄	JOC 50 5696 (1985)
CN	F	py·(HF) _n	J Fluorine Chem 17 565 (1981)



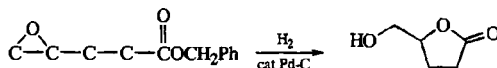
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
CO ₂ H	OR	NaOR	SL 766 (1990)
	SPh	NaSPh	JOC 50 1560 (1985)



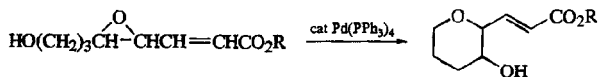
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
	NH ₂	NH ₃	JCS 1116 (1962) CL 1271 (1982) JOC 54 3260 (1989) TL 31 5023 (1990) Tetr 49 6195 (1993)
	NHR	RNH ₂	JCS 1116 (1962) Syn 34 (1990) TL 33 2497, 6735 (1992); 34 1327 (1993)
	NR ₂	R ₂ NH	JOC 50 1560 (1985)
	NHNH ₂	N ₂ H ₄	JOC 54 3260 (1989)
	CO ₂ R	NH ₃	JACS 80 187 (1958)
	N ₃	NaN ₃ , NH ₄ Cl	TL 30 4881 (1989)
		NaN ₃ , HOAc, H ₂ O	Ber 117 1497 (1984)
		<i>i</i> -Pr ₂ NEt·HN ₃	TL 32 667 (1991)
		Mg(N ₃) ₂	CL 809 (1985)
		Me ₃ SiN ₃	TL 36 5417 (1995)
CONR ₂	SPh	NaSPh	JOC 50 1560, 5696 (1985)
	NH ₂	NH ₃	TL 36 4681 (1995)
		NH ₄ OH	TL 36 4681 (1995)
	NHR	RNH ₂	TL 36 4681 (1995)
	NR ₂	R ₂ NH	TL 36 4681 (1995)
	N ₃	Mg(N ₃) ₂	TL 36 4681 (1995)



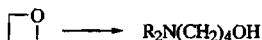
TL 26 5309 (1985)



TL 29 2219 (1988)



TL 31 4747 (1990)



R ₂ NH	JACS 76 2789 (1954)
R ₂ NH, cat M(OTf) ₃ (M = Yb, Gd, Nd)	TL 35 7089 (1994)
R ₂ NH, LiClO ₄	TL 35 7089 (1994)

R_2NH , $LiBF_4$

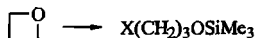
TL 35 761, 7089 (1994)

 R_2NLi

JACS 76 2789 (1954)

 R_2NMgBr

JACS 76 2789 (1954)

 X

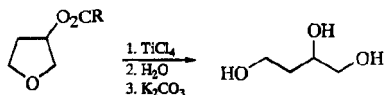
Reagents

 $-CN$ Me_3SiCN , cat Et_2AlCl

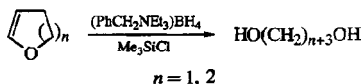
JOC 47 2873 (1982)

 $-N\equiv C$ Me_3SiCN , cat ZnI_2

Syn Commun 15 775 (1985)



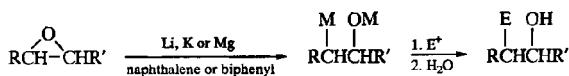
TL 31 1885 (1990)



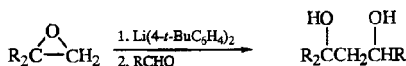
TL 33 6371 (1992)

4. Alkylation of Cyclic Ethers

4.1. Epoxides

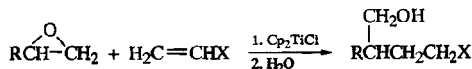
 $E^+ = H_2O, D_2O, RX, CO_2, RSSR$

Angew Int 25 653 (1986)



JOC 55 1528 (1990)

TL 34 5553 (1993)





 $X = COR, CO_2R, CN$

JACS 111 4525 (1989); 116 986 (1994)



TL 32 1059 (1991)

Review: *Org Rxns* 41 135 (1992) (organocopper reagents)For RM = LiCHRX (X = COR, CO₂⁻, CO₂R, CONR₂, CN), see page 1476, Section 2, and page 1717, Section 5.RM

- Li, naphthalene/R₃P·CuI (R = *n*-Bu, Ph)/RX
(R = 1° alkyl, aryl) JOC 52 5057 (1987); 58 2483 (1993)
(intramolecular)
TL 29 6753 (1988) (intramolecular)
- Li, naphthalene/ThCu(CN)Li/RX (RX = 1° RBr, ArI) JOC 58 2492 (1993) (inter- and intramolecular)
- Li, naphthalene/CuCN·LiCl/allylic chloride/
2 MeLi JACS 114 5110 (1992)
- CH₃Li JACS 92 4979 (1970)
TL 27 5335 (1986); 30 6563 (1989)
JOC 52 4505 (1987)
- MeLi, 12-crown-4 TL 30 6563 (1989)
- RLi, BF₃·OEt₂ (R = 1° alkyl, aryl, allylic, benzylic,
vinylic) JACS 106 3693 (1984); 112 323 (1990); 114
671 (1992)
TL 32 769 (1991)
JOC 56 5161 (1991); 58 7768 (1993)
-  Li (intramolecular) JOC 47 3211 (1982)
- ArCH(SiR₃)Li TL 35 8731 (1994)
- PhCH(OMe)Li JACS 113 939 (1991)
- PhCH₂OCH₂Li, BF₃·OEt₂ JOC 60 7778 (1995)
-  TL 35 517 (1994)
-  JACS 111 1381 (1989)
- PhSCH₂Li JOC 60 2022 (1995)
-  TL 23 2379 (1982)
- RCH(Li)SPh JACS 115 3855 (1993)
- (PhS)₂CHLi JACS 115 3855 (1993)



	JACS 106 2949 (1984)
PhSCH(Li)SiMe ₃	TL 27 4403 (1986)
LiCH ₂ SOPh	TL 32 1385 (1991)
RCHLiSO ₂ Ar	JOC 57 5292 (1992); 59 5794 (1994) TL 36 5815 (1995)
Me ₃ SiCHRCHLiSO ₂ Ph	TL 32 1073 (1991)
RCHLiSO ₂ Ph, BF ₃ ·OEt ₂	TL 27 6345 (1986); 36 7101 (1995) CC 1226 (1987) JOC 57 5060 (1992)
RC(Li) ₂ SO ₂ Ph	JACS 109 6205 (1987) TL 31 3279 (1990) JOC 58 1496 (1993)
RCH=CHCH(Li)SO ₂ Ph	JACS 110 5216 (1988)
RSO ₂ C(Li) ₂ CO ₂ R	TL 30 7029 (1989) (intramolecular)
LiCH ₂ COCH(Na)SO ₂ Ar	SL 282 (1990)
LiCH ₂ CO ₂ Li	See page 1717, Section 1.
LiCH ₂ CO ₂ R	See page 1724, Section 2.
LiCH ₂ CONR ₂	See page 1778, Section 4.
LiCH ₂ CN	See page 1801, Section 6.
H ₂ C=CHCH ₂ Li	JACS 108 8015 (1987) JOC 52 862 (1987)
Me ₃ SiCH=CHCH ₂ Li	TL 29 4281 (1988)
H ₂ C=C(SiMe ₃)CH ₂ Li	JOC 59 4138 (1994)
Me ₃ SiC≡CCH ₂ Li	JACS 97 3258 (1975)
(i-Pr) ₃ SiC≡CCH ₂ Li	TL 23 719 (1982)
ArLi	JOC 52 5668 (1987) TL 28 861 (1987)
ArLi, BF ₃ ·OEt ₂	JOC 57 7115 (1992)
PhLi, CuCN	TL 28 1783 (1987)
RCH=CRLi	JACS 113 1704 (1991); 114 5018 (1992)
RCH=CRLi, BF ₃ ·OEt ₂	JACS 113 1704 (1991) TL 32 769 (1991)
RCH=CHLi, MgBr ₂	JOC 52 4495 (1987)
RCH=CHLi, cat CuI	JACS 109 5437 (1987)
RCH=C(OR)Li	See page 351, Section 1.

RM $\text{H}_2\text{C}=\text{CHCH}=\text{C}(\text{OEt})\text{Li}$

JOC 59 3494 (1994)

 $\text{HC}\equiv\text{CLi}$

JOC 53 1184 (1988)

 $\text{HC}\equiv\text{CLi}(\text{EDA}), \text{DMSO}$

Compt Rend C 265 839 (1967)

JCS D 674 (1969)

CC 223 (1973)

JACS 101 5364 (1979); 103 7520 (1981)

JOC 51 4840 (1986)

TL 30 1583 (1989)

 $\text{RC}\equiv\text{CLi}$

Syn 26 (1978); 490 (1981)

Helv 65 385 (1982)

TL 23 1331 (1982)

JACS 106 3548 (1984); 109 6176 (1987)

JOC 54 2409 (1989); 55 2962 (1990); 58 7170 (1993)

 $\text{RC}\equiv\text{CLi}, \text{LiClO}_4$

TL 32 6617 (1991)

 $\text{LiO}_2\text{CC}\equiv\text{CLi}$

TL 3173 (1976)

 $\text{RO}_2\text{CC}\equiv\text{CLi}, \text{BF}_3\cdot\text{OEt}_2$

TL 31 3325, 3619 (1990)

 $\text{RC}\equiv\text{CLi}, \text{BF}_3\cdot\text{OEt}_2$

TL 24 391 (1983); 27 4991 (1986); 28 391, 5457 (1987); 29 865 (1988); 32 6617 (1991)

JOC 52 622, 2860 (1987); 53 265 (1988); 54 2409

(1989); 55 2962 (1990); 58 3516 (1993); 59 1389 (1994); 60 1170 (1995)

JACS 109 7495 (1987); 112 5583 (1990); 117 197 (1995)

SL 701 (1990); 295 (1994)

 PhCM_2K

JOC 58 4656 (1993)

TL 34 803 (1993)

SL 972 (1994)

allylic K

Helv 59 453 (1976)

 RMgX

Org Syn Coll Vol 1 306 (1941)

Chem Rev 49 413 (1951); 59 737 (1959)

JOC 16 673 (1951); 46 4608 (1981); 52 4505 (1987)

Rec Trav Chim 87 1249 (1968)

JACS 92 4979 (1970)

J Chem Res (S) 162 (1982)

TL 27 5335, 6071 (1986)

 ArMgX

TL 32 883 (1991)

 $\text{H}_2\text{C}=\text{CHCH}_2\text{MgX}$

TL 27 5335, 6071 (1986)

Org Syn Coll Vol 7 501 (1990)

 $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{Mg}$

TL 35 711 (1994)

 $(\text{H}_2\text{C}=\text{CH})_2\text{Mg}$


JOC 54 777 (1989)

 $\text{H}_2\text{C}=\text{CHC}(=\text{CH}_2)\text{MgCl}$

JOC 44 4788 (1979)

Me ₂ Mg	TL 23 1763 (1982) JOC 53 4542 (1988)
RMgX, cat CuCN	TL 27 2679 (1986)
MeMgCl, cat CuCl·SMe ₂	TL 28 3835 (1987)
ArMgX, cat CuCl	Org Syn Coll Vol 8 516 (1993)
RMgX, cat Li ₂ CuCl ₄	JOC 54 1295 (1989) SL 889 (1992)
RMgX, cat CuBr·SMe ₂	JOC 58 5690 (1993)
ArMgX, cat CuBr, HMPA	JOC 60 8081 (1995)
RMgX, cat CuI	TL 1503 (1979); 23 1267 (1982); 31 7031 (1990) Can J Chem 61 1166 (1983) CC 620 (1986) JOC 54 1295 (1989); 56 1386 (1991); 60 41 (1995)
RMgX, CuI	CC 836 (1986); 429 (1987) JOC 51 2230 (1986) TL 27 6071 (1986); 28 2627 (1987); 32 883 (1991)
H ₂ C=CHCH ₂ MgCl, cat CuBr	JOC 60 1170 (1995)
H ₂ C=CHCH ₂ MgX, CuI	TL 27 6071 (1986)
H ₂ C=CHMgBr, CuI	TL 27 4485, 5791 (1986) CC 877 (1987) JACS 110 4672 (1988)
R ₂ CuMgX	TL 28 1781, 1993 (1987)
(RCH=CH) ₂ CuMgX	TL 28 1993 (1987) JOC 54 777 (1989)
Cu-polymer/RX (R = 1° alkyl)	JOC 55 788 (1990)
R ₂ CuLi	JACS 92 3813, 4979 (1970); 109 8105 (1987) JOC 38 4263 (1973); 40 2263 (1975) (α-silyl epoxides); 48 546 (1983); 52 4495 (1987); 53 4542 (1988); 57 1713 (1992) Org Rxs 22 253 (1975) JCS Perkin 1 2885 (1982) TL 27 6071 (1986); 28 1781, 1993, 6191 (1987); 30 6563 (1989); 32 883 (1991)
(LiOCH ₂ CMe ₂ CH ₂) ₂ CuLi	JOC 54 5657 (1989)
R ₂ CuLi·2RLi	TL 21 4365 (1980)
(R ₂ C=CR) ₂ CuLi	TL 26 5837 (1985); 27 2519, 5277 (1986); 28 1781, 1993 (1987) JACS 111 1351 (1989)
[R'C≡CCuR]Li, BF ₃ ·OEt ₂	TL 30 4517 (1989); 32 769 (1991)
[(R'C≡C)Cu(CH=CHR)]Li	JCS Perkin I 2954 (1979); 852 (1980) See also page 452, Section 2.28.

RM

$(\text{Me}_3\text{SiC}\equiv\text{CCuCH}_2\text{CH}=\text{CROSiMe}_3)\text{Li}$	JACS 107 5495 (1985)
$\text{RCu}(\text{CN})\text{Li}$	TL 3407 (1977); 2399 (1978) JOC 60 2044 (1995)
$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$	JACS 104 2305 (1982); 109 6176 (1987) JOC 49 3928 (1984); 55 2771 (1990); 56 5161 (1991); 57 720, 922 (1992)
$\text{R}_2\text{C}=\text{CRCH}_2\text{Cu}(\text{Me})(\text{CN})\text{Li}_2$	TL 34 3063 (1993)
$(\text{R}_2\text{C}=\text{CHCH}_2)_2\text{Cu}(\text{CN})\text{Li}_2$	JACS 112 4063 (1990) TL 31 4539 (1990)
$[\text{H}_2\text{C}=\text{C}(\text{SiMe}_2\text{Ph})\text{CH}_2]_2\text{Cu}(\text{CN})\text{Li}_2$	JOC 59 4138 (1994)
$(\text{RCH}=\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2$	JACS 106 5304 (1984) JOC 52 2838 (1987); 53 4495 (1988) TL 29 5929 (1988)
$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2, \text{BF}_3 \cdot \text{OEt}_2$	TL 29 3045 (1988) (R = 2-furyl)
$(\text{PhCH}_2\text{OCH}_2)_2\text{Cu}(\text{CN})\text{Li}_2, \text{BF}_3 \cdot \text{OEt}_2$	JOC 60 7778 (1995)
$(\text{RCH}=\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2, \text{BF}_3 \cdot \text{OEt}_2$	TL 27 5791 (1986); 29 5929 (1988)
$\text{ThCuR}(\text{CN})\text{Li}_2, \text{BF}_3 \cdot \text{OEt}_2$	TL 25 5959 (1984)
$\text{ThCuR}(\text{CN})\text{Li}_2$	TL 25 5959 (1984); 27 4825 (1986) (R = vinylic); 28 945 (1987); 30 27 (1989) (R = <i>n</i> -Bu ₃ SnCH=CH) JOMC 285 437 (1985) JACS 113 9693 (1991) Org Syn Coll Vol 8 33 (1993) (R = vinyl) SL 761 (1993) (R = vinylic)
$\text{ThCu}(\textit{n}\text{-Bu})\text{Cu}(\text{CN})\text{Li}_2, (\text{RCH}=\text{CH})_2\text{Te}$	SL 671 (1995)
$\text{R}_2\text{Cu}(\text{SCN})\text{Li}_2$	JOC 48 546 (1983)
$\text{RCu}(\text{NCy}_2)\text{Li}$	JACS 104 5824 (1982)
 $\text{NCuR}(\text{CN})\text{Li}_2$	TL 33 1041 (1992)
$\text{RCu}(\text{PPh}_2)\text{Li}$	JACS 104 5824 (1982)
$\text{RCu}[\text{P}(\textit{t}\text{-Bu})_2]\text{Li}$	JACS 110 7226 (1988)
Me_3Al	JOC 53 4542 (1988) TL 30 6563 (1989)
$\text{Me}_3\text{Al}, 12\text{-crown-4}$	TL 30 6563 (1989)
$\text{Me}_3\text{Al}, \textit{n}\text{-BuLi}$	JOC 57 1713 (1992)
$\text{Me}_3\text{Al}, \textit{n}\text{-BuLi}, 12\text{-crown-4}$	JOC 57 1713 (1992)
LiAlMe_4	JOC 53 4542 (1988) TL 30 6563 (1989)

LiAlMe_4 , 12-crown-4	TL 30 6563 (1989)
LiAlMe_4 , MeLi	JOC 53 4542 (1988)
$\text{Et}_2\text{AlCH}_2\text{CO}_2\text{-}t\text{-Bu}$	JOC 41 1669 (1976) Syn 284 (1983)
$E\text{-}i\text{-Bu}_2\text{AlCH=CHR}$	JOC 42 2712 (1977)
$(\text{R}_3\text{AlCH=CRR}')\text{Li}$	Syn 632 (1975); 1034 (1980) CC 17 (1976) SL 326 (1990)
$\text{RC}\equiv\text{CAIR}'_2$ ($\text{R}' = \text{Me, Et}$)	CC 634 (1968); 287 (1975); 907 (1976) TL 1379 (1969); 2695 (1970); 3899 (1973); 1769 (1976); 29 901 (1988) JACS 94 4342, 4343 (1972); 95 7171 (1973); 100 3950 (1978); 103 7520 (1981); 108 5559 (1986); 109 2205 (1987); 110 4672, 8223 (1988) JOC 41 1669 (1976); 42 394 (1977); 43 353 (1978); 50 3923 (1985); 55 2962 (1990) JCS Perkin I 2954 (1979); 852 (1980)
$(t\text{-Bu})\text{Me}_2\text{SiCH}_2\text{C}\equiv\text{CAIEt}_2$	JOC 52 4495 (1987)
$\text{MeOAl(R)C}\equiv\text{CR}$	TL 3899 (1973); 31 4489 (1990)
$(\text{RC}\equiv\text{CAIMe}_3)\text{Li}$	JOC 59 8307 (1994)
$(\text{RC}\equiv\text{CAIMe}_3)\text{Li}$, $\text{BF}_3\cdot\text{OEt}_2$	TL 31 7145 (1990)
$[\text{Me}_2\text{Al(C}\equiv\text{CR)}_2]\text{Li}$	JOC 50 3923 (1985) JACS 114 8464 (1992)
RSiMe_3 ($\text{R} = \text{allylic}$), $\text{BF}_3\cdot\text{OEt}_2$	Can J Chem 61 214 (1983) TL 28 2753 (1987) JOC 54 3114 (1989) (all intramolecular)
$\text{H}_2\text{C}=\text{C}(\text{SiMe}_3)\text{CH}_2\text{SiMe}_3$, EtAlCl_2	JOC 59 4138 (1994)
RSiMe_3 ($\text{R} = \text{allylic}$), SnCl_4	TL 30 4845 (1989) (intramolecular)
RSiMe_3 ($\text{R} = \text{allylic}$), TiCl_4	Syn 446 (1978) TL 24 5661 (1983) CC 585 (1984) (intramolecular) JOC 54 3114 (1989) (intramolecular); 55 4849 (1990); 59 4138 (1994)
$\text{H}_2\text{C}=\text{C}=\text{CHCH}_2\text{SiMe}_3$, TiCl_4 [$\text{R} = \text{H}_2\text{C}=\text{CHC}(\text{=CH}_2)\text{-}$]	JOC 55 4849 (1990)
$\text{RSn}(n\text{-Bu})_3$ ($\text{R} = \text{allylic}$), $\text{BF}_3\cdot\text{OEt}_2$	JOC 54 3114 (1989) (intramolecular); 55 4849 (1990) SL 167 (1995)
$\text{RSn}(n\text{-Bu})_3$ ($\text{R} = \text{allylic}$), EtAlCl_2	JACS 115 9305 (1993) JOC 59 4138 (1994)
$\text{RSn}(n\text{-Bu})_3$ ($\text{R} = \text{allylic}$), SnCl_4	SL 691 (1990) (intramolecular)

RMR₃Sn(*n*-Bu)₃ (R = allylic), TiCl₄

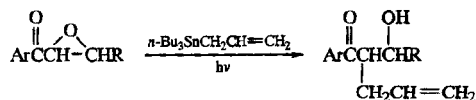
JOC 54 3114 (1989) (intramolecular)

RMnCl, cat Li₂CuCl₄

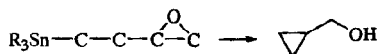
SL 45 (1993)

R₃MnLi

TL 27 5351 (1986)



TL 32 2029 (1991)

BF₃·OEt₂

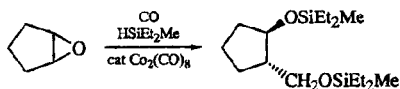
JACS 92 6990 (1970)

JOMC 73 237 (1974); 159 255 (1978)

Syn Commun 17 781 (1987)

EtAlCl₂

JOC 56 2066, 2076 (1991)



JACS 106 6093 (1984)

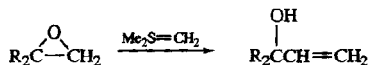


JCS 5404 (1964) (intramolecular)

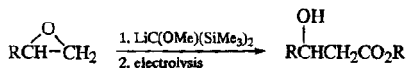
Tetr 25 1807 (1969)

JOC 48 2449, 4572 (1983); 52 425 (1987); 53 3309 (1988) (all intramolecular); 60 41 (1995)

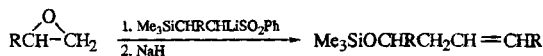
TL 31 7031 (1990)



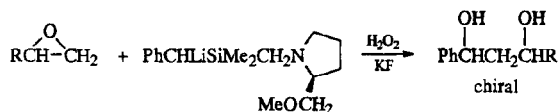
TL 35 5449 (1994)



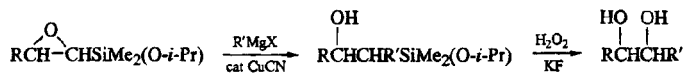
TL 30 219 (1989)



TL 32 1073 (1991)



JOC 57 6107 (1992)



JOC 52 4412 (1987)

R'MPhSeCHSiMe₃

TL 24 4539 (1983)

LiC≡CCH₂OTHPTL 24 4539 (1983)
JOC 50 5687 (1985)LiC≡CCH₂OTHP·BF₃·OEt₂

TL 29 681 (1988)

RMgX, cat CuI

JOC 58 3277 (1993)

R₂Cu(CN)Li₂

TL 32 4817 (1991)

Me₂CuLi

JOC 50 5687 (1985)

R'M

LiC≡CH·EDA

CC 874 (1986) (mixture)



TL 27 4825 (1986)

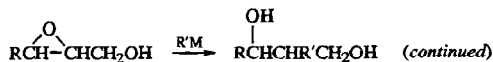
RMgX, cat CuI

JOC 48 3131 (1983)
JACS 108 1035 (1986)
SL 42 (1989)
Tetr 46 7703 (1990)R'₂CuLiJOC 38 4346 (1973) (cyclohexyl system); 52
2596 (1987)
TL 4343 (1979); 23 707 (1982); 24 1377 (1983);
28 5009 (1987); 29 5285 (1988); 31 1443, 2043
(1990)
Tetr 37 3873 (1981)
JACS 112 1626, 6339 (1990); 115 7152 (1993)Me₂CuLi, BF₃·OEt

TL 28 1139 (1987) (on trityl ether)

Me₃CuLi₂

JOC 52 685 (1987) (mixture)

R'M**MeCu(CN)Li**

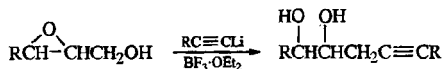
JOC 51 956 (1986) (mixture)

Me₂Cu(CN)Li₂

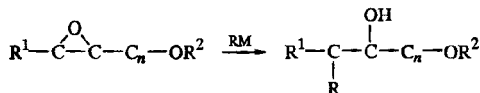
JACS 108 2776 (1986)

TL 28 5009 (1987)

JOC 52 3784 (1987)



CC 202 (1984)

nR²RM

1

H

H₂C=CHCH₂MgCl
R₃Al

JACS 110 2506 (1988)

TL 23 3597 (1982); 24 1377 (1983);

27 3369, 4601 (1986); 28 1139

(1987); 31 2043 (1990); 34 5343,

7111 (1993)

JOC 52 2596 (1987); 57 5060

(1992)

Tetr 44 1035 (1988)

JACS 117 2479 (1995)

TL 33 3375 (1992)

SL 306 (1992)

TL 23 3597 (1982)

JOC 52 685 (1987) (mixture)

JOC 51 956 (1986) (mixture)

TL 28 5009 (1987)

JOC 38 4346 (1973) (cyclohexyl
system)

JOC 48 409 (1983)

Angew Int 21 71 (1982)

JOC 48 409 (1983)

TL 31 7145 (1990)

TL 31 7145 (1990), 34 6407 (1993)

JOC 53 4730 (1988)

SL 266 (1992)

TL 31 7145 (1990)

SL 266 (1992)

CC 1237 (1986)

TL 32 4925 (1991)

JOC 58 5666 (1993)

2

H

RC≡CAIEt₂

JOC 58 5666 (1993)

Me

Me₂CuLi

JOC 54 3588 (1989)

CH₂Ph**Me₃Al, cat n-BuLi or LiOMe**

Angew Int 21 71 (1982)

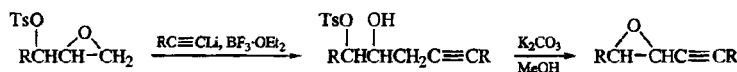
Me₃Al-n-BuLi

JOC 54 3006, 3588 (1989)

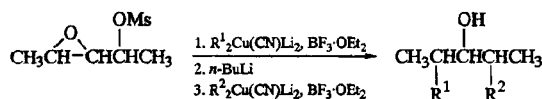
SiMe ₂ (<i>n</i> -Bu)	Et ₃ Al- <i>n</i> -BuLi	JOC 54 3588 (1989)
	Me ₂ CuLi	JOC 54 3588 (1989)
	Me ₃ Al- <i>n</i> -BuLi	JOC 54 3588 (1989)
	Me ₂ CuLi	JOC 54 3588 (1989)



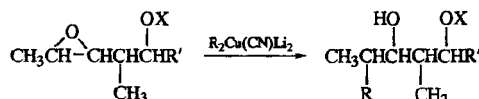
JOC 57 5031 (1992)



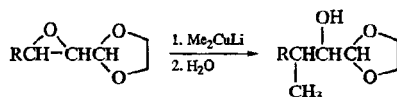
JOC 58 5153 (1993)



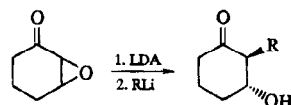
TL 28 5631 (1987)

X = H, SiR₃

TL 28 6195 (1987)

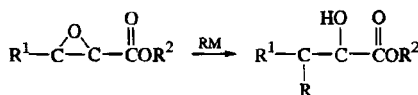


JOC 50 5696 (1985)



JACS 103 2114 (1981)

JOC 54 3374 (1989)

R²

H

Et

alkyl

RM

n-Bu₂CuLi or R₂Cu(CN)Li₂
(R = *n*-Bu, Ph)Me₂CuLiEt₂AlC≡CR

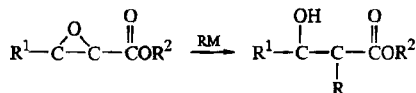
TL 26 4683 (1985)

JACS 106 2949 (1984) (R¹ = CO₂Et)

TL 23 2331 (1982); 27 5397 (1986)

JOC 47 3941 (1982)

JACS 108 5559 (1986)

R²

H

alkyl

RM*n*-Bu₂CuLi, R₂Cu(CN)Li₂ (R = *n*-Bu, Ph)R₂CuLi

TL 26 4683 (1985)

JACS 92 3813 (1970); 106 2949 (1984)

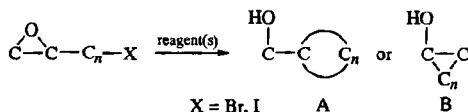
(R¹ = CO₂Et)

JOC 38 4263, 4346 (1973)

TL 32 4477 (1991)



TL 36 307 (1995)

Reagent(s)*n*-BuLi*sec*-BuLi*t*-BuLiCu, *n*-Bu₃PProduct-*n*

A-4, 5; B-4

A-5

A-3-6; B-5, 6

B-6

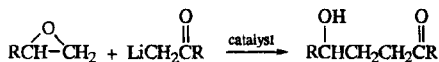
JOC 43 3800 (1978); 45 922

(1980); 47 3211 (1982)

TL 25 4323 (1984)

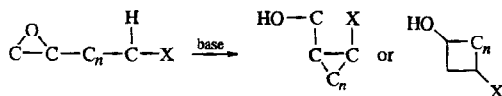
TL 26 3643 (1985)

JOC 52 5057 (1987)

CatalystLiClO₄Yb(OTf)₃

TL 32 7583 (1991)

TL 35 6537 (1994)



Reviews:

Russ Chem Rev 39 265 (1970); 41 403 (1972)

Tetr 39 2323 (1983)

Syn 629 (1984)

XPh₂

vinylic

Ring size

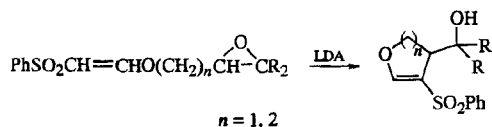
3

3

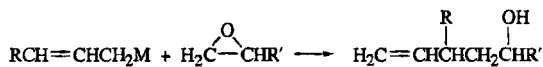
JOC 41 885 (1976)

Tetr 34 1691 (1978)

CH=CHCH=CH	3	TL 1119 (1963)
COR	3-6	JCS 2988 (1951) IACS 79 3519 (1957); 86 3162 (1964); 94 7132 (1972); 107 1438 (1985) (β -lactam) JOC USSR 3 502 (1967); 5 1168 (1969) Israel J Chem 9 63 (1971) TL 3731 (1970); 3683 (1972) Tetr 28 5525, 5533 (1972) JOC 37 2911 (1972) Can J Chem 55 1629 (1977) SL 431 (1990)
CO ₂ R	3	JOC USSR 5 530, 1168 (1969) JOC 41 885 (1976) TL 2441 (1976)
	4	TL 29 816 (1988) (β -lactam)
(CO ₂ R) ₂	3	JOC USSR 2 1163 (1966); 5 1168 (1969)
	5	JOC 34 4060 (1969)
CONR ₂	3	TL 23 1343 (1982) JOC 49 2682 (1984)
	6	JOC 52 4044 (1987)
CN	3-6	IACS 96 5268, 5270 (1974) TL 585 (1975); 30 4767 (1989); 32 2637 (1991) JOC 41 3648 (1976); 57 6301 (1992) SL 723 (1992)
(CN) ₂	3	JOC USSR 4 1700 (1968)
CN, SO ₂ Ph	3, 5, 6	JOC 59 1518 (1994)
SO ₂ Ar	3-6	JOC 41 3648 (1976); 44 4603 (1979); 47 2564 (1982); 50 2943 (1985); 51 5311 (1986); 52 4614 (1987); 55 3962 (1990); 56 4513 (1991) TL 503 (1976); 22 4339 (1981); 26 6301 (1985); 29 6493 (1988); 31 6205 (1990) Can J Chem 56 505 (1978); 59 1415 (1981)
(SO ₂ Ph) ₂	3, 5-7	CC 406 (1987) JOC 56 3530 (1991); 59 1518 (1994)
S(CH ₂) ₃ S	3, 4, 6, 7	JOC 56 6038 (1991); 59 6063, 6069 (1994)
⁺ PPh ₃	4, 5, 7	TL 789 (1977)

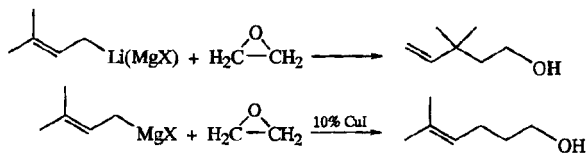


JOC 56 3556 (1991)

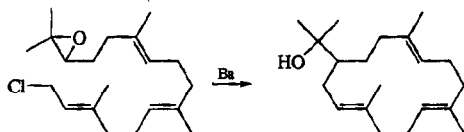


M = Li, Na, MgX, ZnX

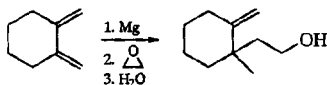
JOMC 69 1 (1974)



TL 4069 (1978)

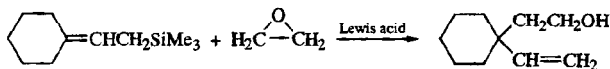


TL 33 6435 (1992)



TL 34 6011 (1993)

JOC 60 5143 (1995)



Lewis acid

$\text{BF}_3 \cdot \text{OEt}_2$

Can J Chem 61 214 (1983) (intramolecular)

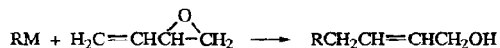
TL 28 2753 (1987) (intramolecular)

TiCl_4

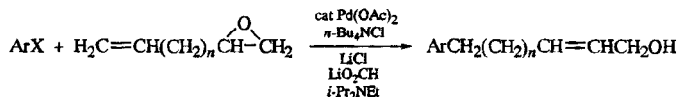
Syn 446 (1978)

TL 24 5661 (1983)

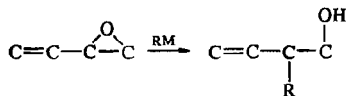
CC 585 (1984) (intramolecular)



See page 236, Section 8.



JOC 55 6244 (1990)

**RM**

RMgX

CC 248 (1969)
 BSCF 2556 (1970)
 TL 2005 (1971)
 JOC 51 1687 (1986)
 SL 719 (1991)

RMgX, cat CuI

JOC 59 4037 (1994)

Me₃Al

JOC 56 6483 (1991)
 CL 1101 (1992)
 TL 34 2969, 6285 (1993)

Et₂AlCH₂CO₂-*t*-Bu

Syn 284 (1983)

LiAlR₄

TL 23 4697 (1982)

R₂CuLi

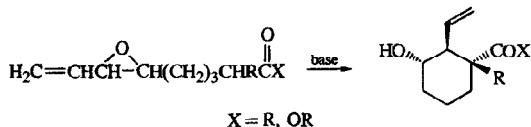
TL 23 4697 (1982)
 JOC 59 4037 (1994)

R₂Cu(CN)Li₂

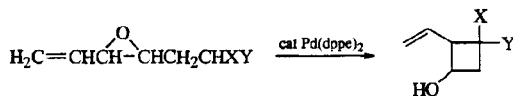
TL 23 4697 (1982)

H₂C=C(SiMe₃)CH₂ZnCl

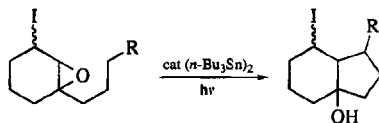
SL 279 (1993)



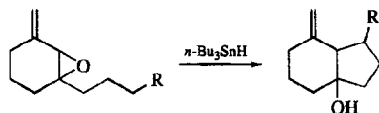
JACS 112 1661 (1990)

X, Y = COR, CO₂R; CO₂R, CO₂R; CO₂R, PO(OR)₂; CN, CN

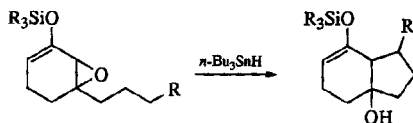
TL 36 2487 (1995)



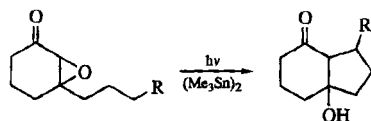
TL 33 4687 (1992)



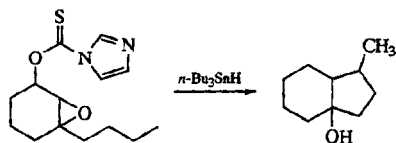
JACS 113 5106 (1991)



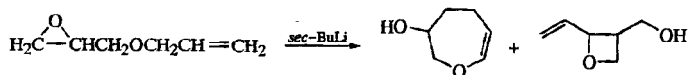
TL 33 7391 (1992)



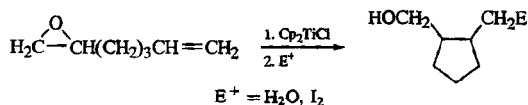
TL 34 2899 (1993)



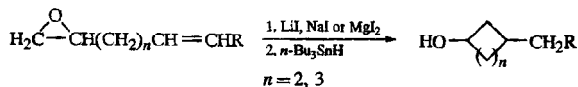
JOC 55 5181 (1990)



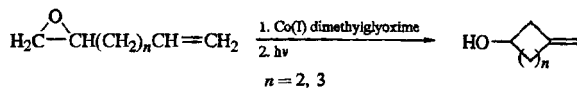
TL 31 3501 (1990)



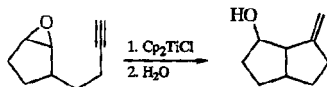
JACS 110 8561 (1988)



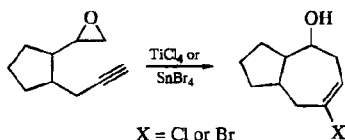
TL 31 5369 (1990)



TL 32 243 (1991)

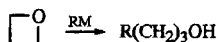


TL 36 15 (1995)



TL 36 7145 (1995)

4.2. Oxetanes



RM

RLi

JACS 73 124 (1951)

RCH(Li)SPh

JACS 115 3855 (1993)



JACS 111 1381 (1989)

H₂C=CRLi

JACS 113 2686 (1991)

RLi, BF₃·OEt₂ (R = 1° alkyl, aryl, vinylic)

JACS 106 3693 (1984)

TL 30 2567 (1989)

RC≡CLi, BF₃·OEt₂

Tetr 40 4261 (1984)

TL 29 4001 (1988); 30 2567 (1989)

RMgX

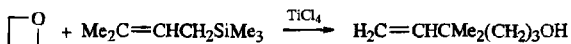
JACS 73 124 (1951); 109 7280 (1987)

RMgX, cat CuI (R = 1° alkyl, allylic, aryl)

TL 1503 (1979); 31 2595 (1990)

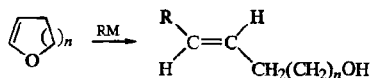
R₃Al

JACS 115 10695 (1993)



JOC 50 2782 (1985)

4.3. Larger Rings



RM

n

R

RLi

1

1° alkyl

TL 32 5903 (1991)

2

1°, 3° alkyl

Can J Chem 41 2600
(1963)

TL 32 5903 (1991)

RLi, CuI

1

1° alkyl, aryl

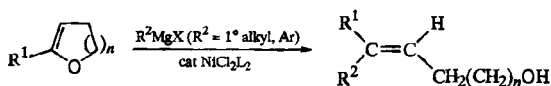
CL 1641 (1982)

RMgX

2

1° alkyl, aryl

JACS 76 4538 (1954)



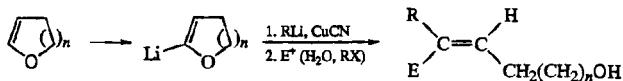
$n = 1, 2$

JACS 101 2246 (1979)

JOC 49 4894 (1984); 50 719 (1985); 54 1215 (1989)

CC 241, 429 (1987)

TL 29 2353, 2357, 2867 (1988); 31 2595 (1990)

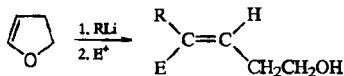


$n = 1, 2$

JACS 111 2363 (1989)

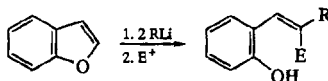
TL 31 1637 (1990); 35 7767 (1994)

JOC 60 3592 (1995) (R = vinylic, $n = 1$)



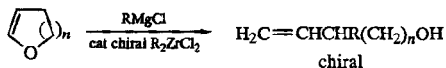
$\text{E}^+ = \text{H}_2\text{O, D}_2\text{O, MeI, CO}_2$

TL 32 5903 (1991)



$\text{E}^+ = \text{H}_2\text{O, D}_2\text{O, RI, CO}_2$

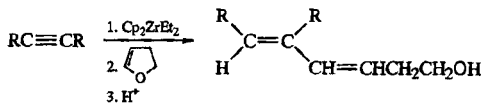
TL 32 5903 (1991)



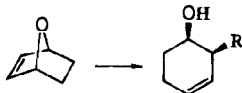
chiral

$n = 1-3$

JACS 115 6997, 8485 (1993); 117 2943, 7097 (1995)



JACS 117 5871 (1995)



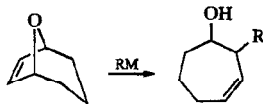
Review: SL 177 (1993)

RI (R = benzylic, aryl, vinylic), cat $\text{PdCl}_2(\text{PPh}_3)_2$,
Zn, Et_3N TL 34 4019 (1993)

ArX (X = I, OTf), Pd catalyst, NaO_2CH TL 36 2051 (1995)

RLi JOC 36 2874 (1971); 59 3906 (1994)
JACS 96 6929 (1974)
TL 30 6437 (1989); 31 1475 (1990); 33 2661 (1992);
34 773 (1993)

$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$ TL 30 6817 (1989); 31 3253 (1990)



Review: SL 177 (1993)

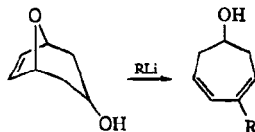
RM

RLi

JOC 55 5305 (1990); 59 3906 (1994)
TL 33 2617 (1992); 34 773, 7451 (1993)
JACS 117 1954 (1995) (intramolecular)

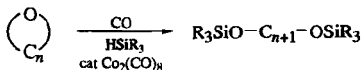
$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$

TL 30 6817 (1989)



TL 34 4591 (1993)

4.4. Various Rings

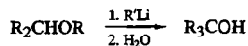


$n = 2-5$

JACS 111 7938 (1989)

5. Rearrangement

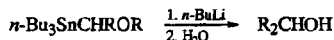
See also page 1281, Section 4.



TL 2809 (1968)
Angew Int 9 763 (1970) (review)
Tetr 45 1409, 2649 (1989)



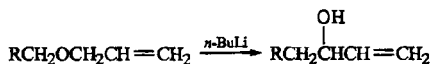
JOC 47 5051 (1982)



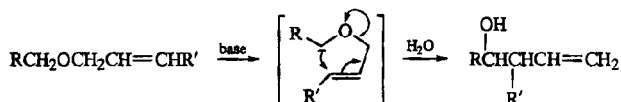
TL 34 8139 (1993)



TL 34 2343 (1993)



TL 28 1043 (1987); 32 2629 (1991)



See also page 236, Section 8.

Reviews:

Angew Int 18 563 (1979) (stereochemistry of 2,3-sigmatropic rearrangements)

Chem Rev 86 885 (1986)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),

Vol 3, Part 3.11, p 975

Org Rxn 46 105 (1994)

R

—

JACS 100 1927 (1978); 108 3841 (1986); 109 3017, 6199 (1987)

TL 26 5013, 5017 (1985); 28 2099, 4993 (1987); 29 6901 (1988); 31 4301, 4425 (1990); 32 5401 (1991); 33 5795 (1992); 34 5217 (1993); 35 9021 (1994)

JOC 52 2960 (1987); 57 1072 (1992)

SL 845 (1992); 391 (1993); 228 (1994)

aryl

CC 4 (1970)

JACS 93 3556 (1971); 113 5402 (1991)

JOC 48 279 (1983); 49 1842 (1984)

TL 29 5409 (1988); 30 2549 (1989); 36 2789 (1995)

vinyl

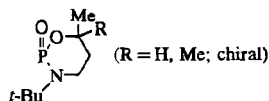
CC 4 (1970)

CL 557 (1977)

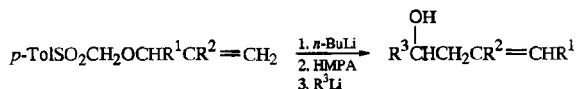
JACS 103 6492 (1981); 107 3915 (1985); 114 5018 (1992)

TL 23 3931 (1982); 29 5409 (1988); 31 2235 (1990); 34 8453 (1993)

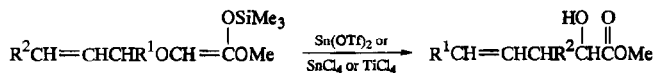
	JOC 48 279 (1983); 49 1707, 1842 (1984); 51 4315 (1986); 53 4108 (1988); 56 1185 (1991); 58 832 (1993) Tetr 42 2911 (1986)
alkynyl	JOC 48 279 (1983); 49 1842 (1984); 51 4316 (1986); 52 3860, 3883 (1987); 53 4108 (1988); 55 227 (1990); 56 3465 (1991); 57 2747, 3085 (1992); 59 324 (1994) CL 1379 (1983) TL 25 565 (1984); 28 723, 3323 (1987); 29 741, 3547, 4588, 5409 (1988); 30 1055 (1989); 31 7353 (1990); 34 5923 (1993); 36 2789, 4073 (1995) Tetr 40 2303 (1984) JACS 110 2925 (1988) SL 527 (1993); 321, 901 (1995)
heterocyclic	TL 24 513 (1983); 25 6011 (1984); 34 749, 753, 8047 (1993); 36 7197, 7201 (1995) JOC 53 4631, 5189 (1988)
COR	Helv 57 2084 (1974)
CR=NNR ₂	JOC 54 5415 (1989) Angew Int 33 2098 (1994) SL 631, 869 (1995)
CO ₂ ⁻	TL 22 69 (1981); 30 4157 (1989) JOC 51 4090 (1986)
CO ₂ R	TL 27 4511 (Me ₃ SiOTf added), 4581 (Cp ₂ ZrCl ₂ added) (1986); 28 803 (1987) (Cp ₂ ZrCl ₂ added); 29 4763 (1988) (Li, Ti, Zr, Hf); 31 2415 (1990) (Cp ₂ ZrCl ₂ added); 32 4647 (1991) (B, Sn enolate); 35 5019 (1994) (chiral B enolate)
CONR ₂	CL 1729 (1985) TL 27 4577 (1986) (Cp ₂ ZrCl ₂ added) JACS 113 6621 (1991)
CN	TL 24 2077 (1974)
PO(OEt) ₂	SL 1035 (1995)
PO(OR) ₂ (R = menthyl, chiral)	TL 36 6635 (1995)



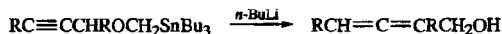
TL 36 6631 (1995)



TL 29 5233 (1988)



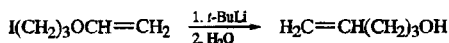
SL 629 (1991)



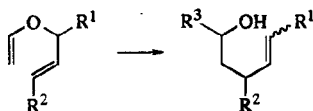
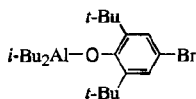
JOC 54 5854 (1989); 56 960 (1991)



JOC 54 5854 (1989); 55 2995 (1990); 56 960 (1991); 57 2747 (1992)

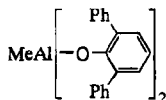


TL 32 4425 (1991)

Reagent*i*-Bu₃Al or *i*-Bu₂AlHR³
HTL 22 3985 (1981)
JOC 56 3841 (1991)

H

JACS 110 7922 (1988); 112 316 (1990)



H

JACS 112 316 (1990)

R³₃AlR³ (R³ = Me, Et)

TL 22 3985 (1981)

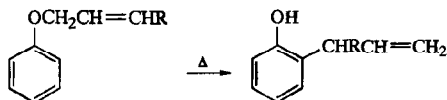
Et₂AlC≡CPh

C≡CPh

TL 22 3985 (1981)

E-(*i*-Bu)₂AlCH=CHC₆H₁₃CH=CHC₆H₁₃

TL 22 3985 (1981)



Org Rxs 2 1 (1944) (review)

Org Syn Coll Vol 3 418 (1955)

Helv 52 335 (1967)

Adv Heterocyclic Chem 8 143 (1967) (review, nitrogen heterocycles); 42 203 (1987) (review, heteroaromatics)

Chimia 24 89 (1970) (review)

Austral J Chem 34 819, 1079 (1981)

CL 1131 (1982)

JOC USSR 18 742, 745 (1982)

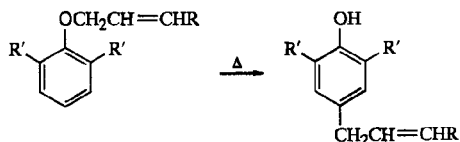
Chem Pharm Bull 30 4539 (1982)

TL, 23 4407 (1982); 27 4945 (1986) (microwave irradiation); 35 2145 (1994); 36 5567 (1995)

Chem Rev 84 205 (1984) (review, catalysis)

CC 182, 750 (1986)

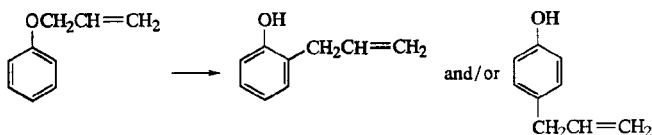
JOC 53 2847, 4515 (1988); 56 2591 (1991); 60 2456 (1995) (microwave irradiation)



Org Rxns 2 1 (1944) (review)

JACS 70 1747 (1948)

JOC 56 2591 (1991)



BF_3 , HOAc

BCl_3

Et_2AlCl

MABR

TiCl_4 , $\text{PhN}=\text{CMeOSiMe}_3$

TiCl_4 , $\text{Ti}(\text{O}-i\text{-Pr})_4$

montmorillonite clay

J Gen Chem USSR 11 722 (1941)

Proc Chem Soc 19 (1957)

Helv Chim Acta 56 14 (1973)

JOC 35 3166 (1970)

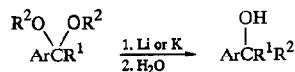
TL 31 377 (1990)

CL 1041 (1975)

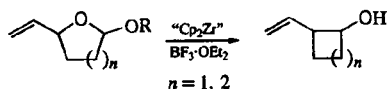
CL 1041 (1975)

TL 31 3241 (1990)

6. Acetal Cleavage

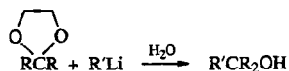


JOC 55 5532 (1990)

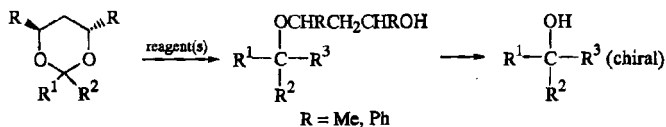



JACS 115 8835 (1993)

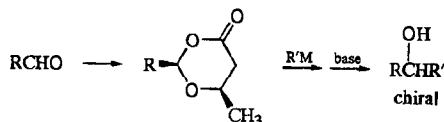
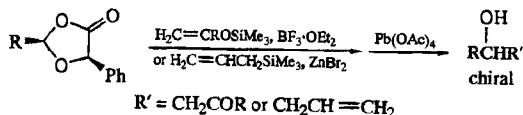
TL 34 7639 (1993)



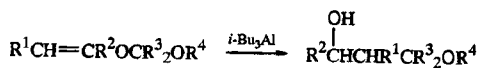
Syn Commun 13 769 (1983)



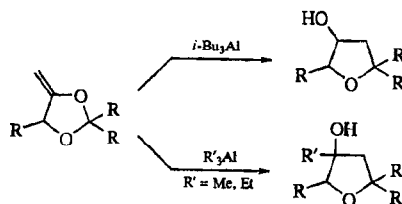
<u>R³</u>	<u>Reagent(s)</u>	
H	Cl ₂ AlH Br ₂ AlH	CC 334 (1987) TL 24 4581 (1983); 27 983, 987 (1986) JOMC 285 83 (1985) CC 334 (1987)
	<i>i</i> -Bu ₂ AlH	TL 24 4581 (1983); 27 983 (1986) JOMC 285 83 (1986)
	TiCl ₄ , Et ₃ SiH	TL 27 987 (1986)
1° alkyl, Ph	R ₂ CuLi·BF ₃	TL 25 3083 (1984)
1° R, H ₂ C=CHCH ₂	RMgX or RLi or R ₂ CuLi(M ₂ X), TiCl ₄	TL 25 3947 (1984)
H ₂ C=CHCH ₂	H ₂ C=CHCH ₂ SiMe ₃ , SnCl ₄ H ₂ C=CHCH ₂ SiMe ₃ , TiCl ₄	JACS 104 7371 (1982) JACS 108 7116 (1986)
	H ₂ C=CHCH ₂ M (M = B  , <i>n</i> -Bu ₃ Sn, Ph ₃ Sn), Lewis acid?	JACS 108 7116 (1986)
H ₂ C=CRCH ₂ (R = H, Me)	H ₂ C=CRCH ₂ SiMe ₃ , TiCl ₄ , Ti(O- <i>i</i> -Pr) ₄	JACS 105 2088 (1983) TL 25 3951 (1984) JOC 50 2598 (1985)
RC≡C	RC≡CSiMe ₃ , TiCl ₄ RC≡CM (M = Me ₃ Si, <i>n</i> -Bu ₃ Sn), Lewis acid?	JACS 105 2904 (1983) JACS 108 7116 (1986)
CH ₃ CH ₂ COCH ₂	CH ₃ CH ₂ COCH ₂ SiMe ₃ , SnCl ₄	JACS 104 7371, 7372 (1982)
RCOCH ₂	H ₂ C=CR ₂ SiMe ₃ , TiCl ₄	JACS 104 7371, 7372 (1982); 106 7588 (1984) JOC 52 180 (1987)
CH ₂ CO ₂ H	H ₂ C=C(O- <i>t</i> -Bu)OSiMe ₂ - <i>t</i> -Bu, TiCl ₄ /CF ₃ CO ₂ H	TL 26 2535 (1985)
CN	NCSiMe ₃ , TiCl ₄	JOC 48 2294 (1983) TL 25 591 (1984)

R'MR'Li (R' = 1° alkyl, aryl, vinyl), CuBr·SMe₂ TL 27 2945 (1986)H₂C=CHCH₂Li, CuBr, BF₃·OEt₂ TL 27 2945 (1986)Me₃SiR' (R' = allyl, alkynyl, CN), Cl₃TiX (X = Cl, O-*i*-Pr) Angew Int 25 178 (1986)

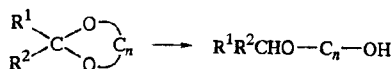
JOC 49 2513 (1984)



JOC 52 5700 (1987)



JACS 117 6394 (1995)

R¹

Ph

R²

H

Reagent(s)*i*-Bu₂AlHn

2, 3

CL 1593 (1983)
Chem Pharm Bull 32 791
(1984)LiAlH₄, AlCl₃

2-4

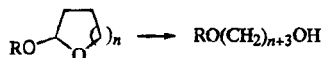
JACS 84 2371 (1962)
JOC 27 67 (1962)
Can J Chem 47 1195 (1969)
Carbohydr Res 44 1 (1975); 51
C19 (1976)
TL 3551 (1976); 22 3919
(1981); 23 3507 (1982)

<i>p</i> -MeOC ₆ H ₄	H	NaBH ₃ CN, CF ₃ CO ₂ H or Me ₃ SiCl	3	CC 201 (1984)
H or alkyl	H or alkyl	LiAlH ₄ , AlCl ₃	2, 3	JACS 84 2371 (1962) JOC 27 67 (1962) Can J Chem 42 990 (1964); 43 1030 (1965); 47 1195 (1969) Org Syn Coll Vol 5 303 (1973)

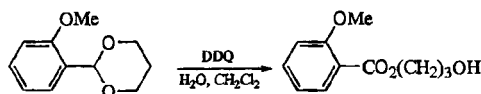


Review: T. W. Greene, "Protective Groups in Organic Synthesis," Wiley-Interscience, New York (1981), pp 72-86

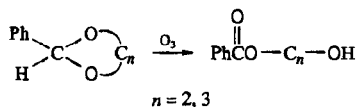
<u>R¹</u>	<u>R²</u>	<u>Reagent(s)</u>	<u>n</u>	
Ph	H	N ₂ H ₄ , H ₂ O, cat Pd-C	2	Syn 317 (1986)
		HCO ₂ H, cat Pd-C	3	Carbohydr Res 83 175 (1980)
		cyclohexene, cat Pd(OH) ₂ -C	3	Syn 396 (1981)
<i>p</i> -CH ₃ OC ₆ H ₄	CH ₃	SnCl ₄ / <i>n</i> -Bu ₄ NOH	2, 3	JOC 46 2419 (1981)



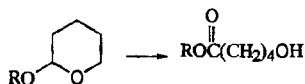
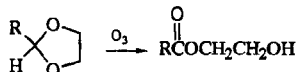
<u>n</u>	<u>Reagents</u>	
1, 2	LiAlH ₄ , AlCl ₃	JOC 30 2441 (1965) Can J Chem 45 2547 (1967)
2	LiAlH ₄ , HCl	JACS 73 5917 (1951)



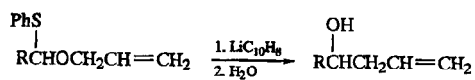
TL 23 889 (1982)



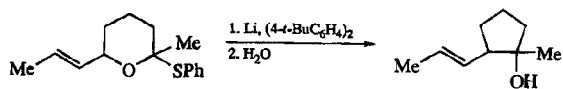
Can J Chem 53 1204 (1975)



Can J Chem 49 2465 (1971)



JACS 111 2981 (1989)

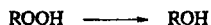


JACS 114 375 (1992)

8. REDUCTION

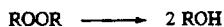
For the reduction of cyclic ethers, see page 1019, Section 2.

1. Peroxides



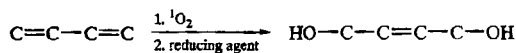
H ₂ , cat Raney Ni	Ann 618 194 (1958)
H ₂ , cat Pd-C	JCS 3312 (1964)
H ₂ cat Pd-CaCO ₃	JCS 2280 (1957)
H ₂ , cat Pt	JCS 665 (1956); 3474 (1958)
H ₂ , cat PtO ₂	JACS 73 2188 (1951); 115 5041 (1993)
NaBH ₄	JCS 3312 (1964) JACS 90 975 (1968); 117 2694 (1995) JOC 37 2631 (1972) Helv 61 2777 (1978)
LiAlH ₄	JACS 75 5011 (1953); 94 2056 (1972); 115 5041 (1993); 117 2694 (1995) JCS 665 (1956); 3474, 4637 (1958) JOC 31 2536 (1966) TL 3715 (1968)
Na, ROH	JOC 15 753 (1950) Ber 91 1910 (1958)
KI	Rec Trav Chim Pays-Bas 96 157 (1977)
SnCl ₂	JCS 665 (1956)
Zn, HOAc	JCS 665 (1956); 3474, 4637 (1958); 1578 (1962) JOC 58 4448 (1993)
NaHSO ₃	JOC 16 113 (1951)
Na ₂ SO ₃	Ber 75 313 (1942); 87 554 (1954) JCS 665 (1956); 3474, 4637 (1958) Helv 54 1822 (1971)
Me ₂ S	JACS 101 275 (1979)

N_2H_4 , H_2O	Ann 618 185 (1958) JOC 28 3217 (1963)
py	Syn Commun 3 45 (1973)
Et_3P	Rec Trav Chem Pays-Bas 96 157 (1977)
<i>n</i> - Bu_3P	JACS 82 1393 (1960)
Ph_3P	Ann 591 138 (1955); 618 185 (1958) JCS 4637 (1958) 82 1393 (1960); 112 5193 (1990); 115 3008, 1 (1993); 117 3976 (1995) JACS 57 2076 (1974) JOC 58 4448 (1993) TL 35 1681 (1994)
$(MeO)_3P$	JACS 90 975 (1968)
$(EtO)_3P$	JACS 81 1243 (1959) JOC 25 1000 (1960)



H_2 , cat Pd-C	JOC 53 3338 (1988); 55 4079 (1990)
$LiAlH_4$	JCS 2679 (1952) JACS 75 5011 (1953) Austral J Chem 31 1737 (1978)
Na, ROH	Ber 91 1910 (1958)
Zn, HOAc	JACS 78 136 (1956) TL 169 (1972) Austral J Chem 31 1737 (1978)
CuCl	JOC 54 3383 (1989)
<i>n</i> - Bu_3P	JOC 38 3175 (1973)
Ph_3P	JOC 38 3175 (1973)
H_2NCSNH_2	JOC 54 3383 (1989)

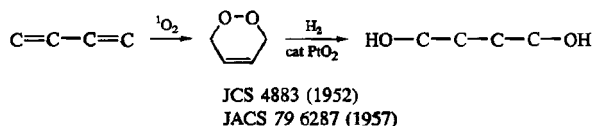
See also the reagents listed in the following equation.



Reducing agent

review	Tetr 47 1343 (1991)
H_2 , cat Pd- $CaCO_3$, Pb(OAc) $_2$, quinoline	JOC 59 2848 (1994)
$NaBH_4$	TL 30 1719 (1989)
$LiAlH_4$	Angew 88 262 (1976) JOC 54 3882 (1989) JACS 112 2749 (1990) SL 609 (1993)

Zn, HOAc	JOC 54 735 (1989); 58 1501 (1993) SL 1243 (1995)
SmI ₂	JOC 54 735 (1989); 58 7185 (1993)
H ₂ NCSNH ₂	Angew Chem 68 248 (1956) Helv 56 2028 (1973) Syn 876 (1974) TL 239 (1975); 30 1719 (1989) JOC 43 2737 (1978); 54 3882 (1989) JACS 101 7537 (1979); 110 4726 (1988) SL 759 (1991); 609, 672 (1993)



2. Aldehydes and Ketones



Reviews:

Syn 605 (1982) (stereoselectivity of reduction of chiral aminocarbonyl compounds)
JACS 110 4475 (1988) (Cram/anti-Cram)

2.1. Hydrogenation

Reviews:

C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley Interscience, New York (1970), p 201
M. Freifelder, "Practical Catalytic Hydrogenation," Wiley Interscience, New York (1971), Chpt 14
H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, New York (1972), p 1
M. Freifelder, "Catalytic Hydrogenation in Organic Synthesis: Procedures and Commentary," J. Wiley & Sons, New York (1978), Chpt 9
P. N. Rylander, "Hydrogenation Methods," Academic Press, New York (1985), Chpt 4
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 1.6, p 139
SL 169 (1992) (enantioselective Rh hydrogenation)

H ₂ , cat Et ₄ N[HCr ₂ (CO) ₁₀]	TL 32 1199 (1991)
H ₂ , FeCl ₂	Helv 69 803 (1986) (5-hydroxy-3-oxoalkanoate ester)
H ₂ , cat RuCl ₂ (PPh ₃) ₃ , cat EDA, cat KOH (C=O > C=C, C≡C)	JACS 117 10417 (1995)
H ₂ , cat RuCl ₂ (CO) ₂ (PPh ₃) ₂ , Δ (aldehydes only)	JOMC 145 189 (1978)

H ₂ , cat RuX ₂ (BINAP) (X = Cl, Br)	JACS 111 9134 (1989) (β -keto esters)
H ₂ , cat [Rh(1,5-hexadiene)Cl] ₂ + R ₃ P (enantioselective)	JOMC 94 C47 (1975)
H ₂ , cat [Rh(1,5-hexadiene)L ₂]X (L ₂ = 2,2'- bipyridine, phenanthrolines; X = PF ₆ , BPh ₄) (C=O > C=C)	JOMC 140 63 (1977)
H ₂ , cat [Rh(bipy)S ₂] ⁺ or [Rh(bipy) ₂] ⁺ (S = solvent) (C=O > C=C)	JOMC 157 345 (1978)
H ₂ cat [Rh(COD)(<i>i</i> -Pr ₂ PC ₅ H ₄ FeC ₃ H ₄ P- <i>i</i> -Pr ₂)]OTf	TL 35 4963 (1994)
H ₂ , cat NaH-NaO- <i>t</i> -Am-Ni(OAc) ₂	JOC 45 1946 (1980)
H ₂ , cat nickel boride or Raney nickel	JOC 46 1263 (1981)
H ₂ , cat Pd-C	JOC 60 2430 (1995)
H ₂ , cat Pt	JOC 53 1218 (1988) (β -keto ester)

2.2. Reduction by Metals

Reviews:

Tetr 42 6351 (1986) (alkali metals in protic solvents)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 8, Part 1.4, p 107

Li, NH ₃	JACS 90 6486 (1968); 108 800 (1986); 110 4475 (1988) JCS C 968 (1969) Helv 64 2109 (1981) Acct Chem Res 16 399 (1983) JOC 57 1968 (1992)
Li, Na, or K; NH ₃	JCS C 968 (1969) BSCF 4399 (1970) JCS Perkin I 999 (1972) Helv 65 402 (1982)
Li, Na or K; NH ₃ ; NH ₄ Cl	BSCF 4404 (1970) JCS Perkin I 999 (1972) Helv 64 2109 (1981); 65 402 (1982) CC 1558 (1986) JACS 110 4475 (1988)
Li, NH ₃ , ROH	BSCF 4404 (1970) Pure Appl Chem 49 1049 (1977) JACS 108 3443 (1986); 111 4852 (1989) JOC 56 338 (1991) TL 32 5219 (1991)
Li, ROH	JCS C 968 (1969)
Na, H ₂ O, EtOH	JACS 106 4547 (1984)
Na, EtOH	JACS 110 4475 (1988)


Na, <i>i</i> -PrOH	JOC 51 4779 (1986) Org Syn 65 203 (1987) Org Syn Coll Vol 8 522 (1993)
Na, ROH	JCS C 968 (1969)
K, ROH	JCS C 968 (1969)
Mg, CuCl ₂ ·2H ₂ O (RCHO only)	TL 36 7119 (1995)
Mg, CdCl ₂ , H ₂ O	TL 34 1681 (1993)
Al(Hg), H ₂ O	Arch Pharm 280 361 (1942) TL 29 525 (1988)
Al, NiCl ₂ ·6H ₂ O (ArCHO and ArCOR only)	TL 30 6567 (1989)
Al or Zn, SbCl ₃ , H ₂ O, DMF (RCHO only)	TL 31 1185 (1990)
Zn, NiCl ₂ ·6H ₂ O, H ₂ O, DMF (RCHO only)	TL 33 5417 (1992)
Zn, cat NiCl ₂ , D ₂ O, dioxane (R ₂ CO only?)	JOC 55 1664 (1990)
Fe, HOAc	Org Syn Coll Vol 1 304 (1932) JACS 61 2134 (1939)


2.3. Metal Hydride Reduction

Reviews and key articles:

- N. G. Gaylord, "Reduction with Complex Metal Hydrides." Interscience, New York (1956)
H. C. Brown, "Boranes in Organic Chemistry," Cornell Univ. Press, Ithaca, NY (1972), pp 209–250
H. O. House, "Modern Synthetic Reactions," Benjamin, New York (1972), p 49
Chem Soc Rev 5 23 (1976)
Tetr 35 449 (1979) (stereochemistry and mechanism)
Topics Stereochem 11 53 (1979) (stereochemistry)
JACS 103 4540 (1981) (stereochemistry of cyclohexanone reductions)
J. Seyden Penne, "Reductions by the Alumino- and Borohydrides in Organic Synthesis,"
VCH-Lavoisier (1991), Chpt 2
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 8, Parts 1.1 and 1.7
TL 34 5483 (1993) (stereochemistry)

LiH	JOC 52 4299 (1987) (2-alkenal, 2-alkynal, alkanone)
LiH, VCl ₃	JOC 43 4804 (1978)
LiH, <i>t</i> -BuOH, Ni(OAc) ₂	TL 36 6051 (1995)
NaH, FeCl ₂ or FeCl ₃	JOC 41 1667 (1976)
NaH, NaO- <i>t</i> -Am, Ni(OAc) ₂	TL 1069 (1977)
NaH, NaOCMe ₂ CH ₂ CH ₂ CMe ₂ ONa, Ni(OAc) ₂	TL 29 1379 (1988)
NaH, NaO- <i>t</i> -Am, MCl ₂ (M = Zn, Cd, Ni, Co, Mn), Me ₃ SiCl	TL 29 1379 (1988)
NaH; <i>t</i> -AmOH; Ni(OAc) ₂ , ZnCl ₂ , MgBr ₂ , CdCl ₂ , CoCl ₂ or MnCl ₂ ; (Me ₃ SiCl)	JOC 55 5911 (1990)


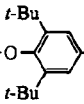
MgH ₂	JOC 43 1557 (1978)
ROMgH	JOC 43 1560 (1978)
ArOMgH	JOC 43 1557, 1560 (1978)
ROMg ₂ H ₃ (R = Me, Ar)	TL 3133 (1977)
R ₂ NMgH	JOC 43 1564 (1978)
BH ₃	JACS 92 1637 (1970); III 2169 (1989)
BH ₃ , cat Ti(O- <i>i</i> -Pr) ₄	TL 35 5141 (1994)
BH ₃ , TiCl ₄	JOC 59 705 (1994) (β -alkoxy ketone, β -keto ester)
BH ₃ ·SMe ₂	Syn 733 (1982)
BH ₃ ·NH ₃	TL 21 693 (1980)
BH ₃ ·NH ₃ , citric acid	Ann 982 (1983) JACS 114 998 (1992)
BH ₃ · <i>t</i> -BuNH ₂	TL 21 693 (1980) JACS 110 3670 (1988); III 278 (1989)
BH ₃ · <i>t</i> -BuNH ₂ , TiCl ₄	JOC 59 705 (1994) (β -alkoxy ketone, β -keto ester)
BH ₃ ·NMe ₃	CL 61 (1986) (ketone on silica gel)
BH ₃ ·NMe ₃ , TiCl ₄	JOC 59 705 (1994) (β -alkoxy ketone, β -keto ester)
BH ₃ ·py	JOC 23 1561 (1958)
BH ₃ ·pyridine polymer	JOC 45 2724 (1980)
BH ₃ ·py, CF ₃ CO ₂ H	Chem Pharm Bull 27 2405 (1979)
BH ₃ ·py, TiCl ₄	JOC 59 705 (1994) (β -alkoxy ketone, β -keto ester)
 NBH ₂	Syn 214 (1981)
(CH ₃) ₂ CHC(CH ₃) ₂ BH ₂	JOC 37 2942 (1972); 39 1631 (1974)
(CH ₃) ₂ CHC(CH ₃) ₂ BHCl·SMe ₂	JOC 51 5264 (1986)
(Sia) ₂ BH	JACS 92 7161 (1970) JOC 39 1631 (1974)
Cy ₂ BH	JOC 39 1631 (1974)
(Ipc) ₂ BH	JACS 88 2871 (1966) JOC 39 1631 (1974)
9-BBN	JOC 40 1864 (1975); 41 1778 (1976); 42 1197 (1977) TL 35 8541 (1994)

9-BBN:py	JOC 42 4169 (1977)
CB	JOC 42 512 (1977); 55 5190 (1990) (β -hydroxy ketones)
CB, cat $\text{Ti}(\text{O}-i\text{-Pr})_4$	TL 35 5141 (1994)
CB, cat $\text{CIRh}(\text{PPh}_3)_3$	JOC 55 5190 (1990) (β -hydroxy ketones)
$(\text{CF}_3\text{CO}_2)_2\text{BH}$	JOC 46 355 (1981)
SiaB 	JOC 43 1470 (1978)
$\text{Et}_3\text{B} / \text{NaBH}_4$	TL 30 5115 (1989) (5-hydroxy-3-oxoalkanoate ester)
LiBH_4	JACS 107 6046 (1985) (2-alkyn-1-one); 111 1396 (1989) (stereochemistry) Ber 118 722 (1985) (β -diketone to 1,3-alkanediol) JOC 52 5067 (1987)
$\text{LiBH}_4, \text{SnCl}_4$	JACS 111 8421 (1989)
NaBH_4	JACS 71 122 (1949); 75 1286 (1953); 84 373 (1962); 88 2811 (1966); 111 1396 (1989) (stereochemistry) JCS C 968 (1969) Tetr 26 2411 (1970); 40 2233 (1984) (on B chelate of β -hydroxy ketones) Ber 118 722 (1985) (β -diketone to 1,3-alkanediol) TL 26 2951 (1985) (on β -chelate of δ -keto- β -hydroxy ester); 28 155 (1987) (on B chelate of β -hydroxy ketone); 33 1759, 2925 (β -keto ester) (1992); 36 7905 (1995) Helv 69 803 (1986) (on B chelate of δ -hydroxy- β -keto ester) JOC 52 4062 (1987) (β -hydroxy ketone); 53 869 (1988) (γ -amido- β -keto ester); 55 99 (1990)
NaBH_4 , alumina	Syn 891 (1978)
NaBH_4 , Fontainebleau sand	CC 1066 (1981)
NaBH_4 , polydibenzo-18-crown-6	TL 32 2157 (1991)
NaBH_4 , phase transfer	CC 641 (1977)
NaBH_4 , HOAc	CC 535 (1975) (aldehydes only) TL 28 4725 (1987)
NaBH_4 , tartaric acid	Syn Commun 14 955 (1984)
NaBH_4 , $\text{PhCH}(\text{OH})\text{CO}_2\text{H}$	Ind J Chem B 21 212 (1982)
NaBH_4 , Et_2BOMe	TL 28 155 (1987) (β -hydroxy ketone); 29 6467 (1988) (β,δ -diketo esters to 3,5-dihydroxyalkanoate esters); 33 7525 (1992) (β -hydroxy- δ -keto ester); 34 513 (1993) (β -hydroxy- δ -keto ester) CL 1923 (1987) (β -hydroxy ketone)

- JOC 56 5752 (1991) (β,δ -diketo ester to 3,5-dihydroxyalkanoate ester); 57 5058 (β -hydroxy ketone), 5596 (1992); 60 7774 (1995) (δ -hydroxy- β -keto ester)
JOC 56 741 (1991) (δ -hydroxy- β -keto ester)
- NaBH₄, Et₃B
TL 31 2545 (1990)
JOC 57 7143 (1992); 58 2523 (1993)
(all δ -hydroxy- β -keto esters)
- NaBH₄, *n*-Bu₃B
CL 1415 (1980) (β -hydroxy ketone diastereoselectivity)
- NaBH₄, CaCl₂
TL 32 6147 (1991) (β -keto esters and amides)
- NaBH₄, Ti(O-*i*-Pr)₄
TL 28 703 (1987) (β -hydroxy ketone)
- NaBH₄, Cp₂TiCl₂
JOC 60 5963 (1995)
- NaBH₄, cat MnCl₂
TL 32 6147 (1991) (β -keto esters and amides)
- NaBH₄, NiCl₂/Me₃SiCl
TL 28 5741 (1987) (aldehydes only)
- NaBH₄, PdCl₂
CL 1029 (1981) (hindered ketones)
- NaBH₄, ZnCl₂
TL 32 6147 (1991) (β -keto esters and amides)
- NaBH₄, ZnBr₂
SL 771 (1990) (α -sulfone)
- NaBH₄; LnCl₃, SmCl₃ or CeCl₃
JACS 100 2226 (1978)
- NaBH₄, CeCl₃
Syn Commun 10 623 (1980)
JOC 51 5320 (1986) (2-alkyn-1-one)
SL 273 (1991) (β -diketone to 3-hydroxy-1-alkanone)
TL 33 6569 (1992) (α,β -epoxy ketones); 35 6469 (1994); 36 7905 (1995)
- KBH₄
JOC 50 2668 (1985)
- KBH₄, *N*-dodecyl-*N*-methylephedrenium bromide, H₂O, C₆H₆
Syn 531 (1975)
- Ca(BH₄)₂
TL 29 659 (1988) (α -PhS- β -keto esters)
- (Me₄N)BH₄, TiCl₄
JOC 59 705 (1994) (β -alkoxy ketone)
- (Et₄N)BH₄
TL 21 3963 (1980) (aldehyde only)
- (*n*-Bu₄N)BH₄
JOC 41 690 (1976); 45 216 (1980); 55 99 (1990)
TL 28 5661 (1987)
- (*n*-Bu₄N)BH₄, TiCl₄
JOC 59 705 (1994) (β -keto ester)
- N*-dodecyl-*N*-methylephedrenium borohydride on montmorillonite support
TL 32 1247 (1991)
- Cp₂ZrClBH₄
TL 4985 (1978)
- (Ph₃P)₂CuBH₄; HCl, AlCl₃, BF₃·OEt₂ or ZnCl₂
TL 22 675 (1981)


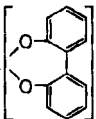
- $\text{Zn}(\text{BH}_4)_2$ JACS 82 6074 (1960); 106 1154 (1984) (β -keto imide); 107 1421 (1985); 108 4603 (1986) (β -keto ester); 111 1396, 8421 (1989) (both stereochemistry); 112 866 (1990) (δ -hydroxy- β -keto imide); 115 11446 (1993) (δ -hydroxy- β -keto imide, β -keto imide)
 Proc Natl Acad Sci USA 72 3355 (1975)
 TL 21 1641 (1980) (β -keto ester); 22 4723 (1981) (α,β -epoxy ketone); 24 2653 (α -hydroxy ketone), 4805 (β -keto imide), 5385 (β -keto amide) (1983); 25 6015 (1984) (chiral, β -keto amides); 26 6465 (1985) (β -keto imide); 27 6341 (1986) (α -hydroxy ketone); 28 5129 (1987); 29 5767 (1988) (α -alkoxy ketones); 33 2361 (1992) (α -nitro ketones); 34 5483 (1993); 35 4891 (1994)
 Syn Commun 13 901 (1983) (α,β -epoxy ketones)
 Acct Chem Res 17 338 (1984) (review)
 Chem Pharm Bull 32 1411 (1984) (β -hydroxy or alkoxy ketone)
 Ber 118 722 (1985) (β -diketone to 1,3-diol)
 Helv 69 803 (1986) (δ -hydroxy- β -keto ester)
 Tetr 48 2127 (1992) (β -hydroxy ketone)
 SL 885 (1993) (review)
- $\text{Zn}(\text{BH}_4)_2, \text{SnCl}_4$ JACS 111 8421 (1989)
- $\text{Zn}(\text{BH}_4)_2, \text{ZnCl}_2$ JACS 109 7488 (1987) (β -keto ester)
- NaBH_3OH JOC 42 3963 (1977)
- NaBH_2S_3 Syn 526 (1972)
- LiBH_3NR_2 TL 35 5201 (1994)
- $\text{LiBH}_3\text{N}(i\text{-Pr})_2$ TL 35 5201 (1994)
 JOC 59 6378 (1994)
- LiBH_3N TL 33 4533 (1992); 35 5201 (1994)
 JOC 59 6378 (1994)
- $\text{NaBH}_3\text{NMe}_2$ JOC 49 2438 (1984)
- LiBH_3CN JACS 91 3996 (1969)
- NaBH_3CN JOC 40 2530 (1975); 53 873 (1988) (γ -alkoxycarbonylamino- β -keto ester)
 Syn 135 (1975)
- $\text{NaBH}_3\text{CN}, \text{CF}_3\text{CO}_2\text{H}$ JOC 45 216 (1980)
- $\text{NaBH}_3\text{CN}, \text{TiCl}_4$ JACS 117 5776 (1995) (β -keto ester)
- $\text{NaBH}_3\text{CN}, \text{ZnCl}_2$ JOC 50 1927 (1985)
- $\text{NaBH}_3\text{CN}, \text{CeCl}_3$ TL 35 6469 (1994)
- $(\text{Et}_4\text{N})\text{BH}_3\text{CN}, \text{TiCl}_4$ JOC 59 705 (1995) (α - and β -alkoxy ketone, β -keto ester and amide)

$[(\text{Ph}_3\text{P})_2\text{CuBH}_3\text{CN}]_2$	TL 21 813 (1980)
LiH_3BMe	Syn Commun 12 723 (1982)
$\text{LiH}_3\text{B}(n\text{-Bu})$	JOC 47 3311 (1982)
$\text{LiH}_3\text{BCRR}'\text{CN}$ (R, R' = H, H; Me, Me; H, Ph)	JOC 55 4464 (1990)
$\text{LiH}_2\text{B}(\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2$	JACS 96 274 (1974)
$\text{K} \left[\begin{array}{c} \text{H} \diagup \text{B} \diagdown \text{O} \\ \text{R} \diagdown \text{O} \end{array} \right]$	JOC 51 337 (1986)
$\text{NaHB}(\text{OR})_3$ (R = Me, <i>i</i> -Pr, <i>t</i> -Bu)	JCS 3426 (1955) JACS 78 3616 (1956) Tetr 26 2411 (1970)
$\text{KHB}(\text{O-}i\text{-Pr})_3$	JOC 49 885 (1984) Ber 118 722 (1985) (β -diketone to 1,3-diol)
$\text{NaHB}(\text{OAc})_3$	CC 535 (1975) (aldehydes only) TL 24 273 (1983) (β -hydroxy ketones); 25 5449 (1984) (β -hydroxy ketones); 35 6469 (1994) (α -alkoxy ketone) JACS 108 2476 (1986); 112 866 (1990) (δ -hydroxy- β -keto imide); 113 5365, 5378 (1991); 115 11446 (1993) (δ -hydroxy- β -keto imide) CC 880 (1987) JOC 55 5192 (1990) (β -hydroxy ketones); 57 2093 (1992) Tetr 48 2127 (1992) (β -hydroxy ketone)
$\text{NaHB}(\text{OAc})_3, \text{CeCl}_3$	JACS 113 9693 (1991)
$\text{KHB}(\text{OAc})_3$	TL 4851 (1979) (aldehydes only)
$(\text{Me}_4\text{N})\text{HB}(\text{OAc})_3$	TL 27 5939 (1986); 30 1037, 6063 (1989) (all β -hydroxy ketones); 33 1605 (3-hydroxy-5-sulfinyl-1-alkanone), 4233 (β -hydroxy ketone) (1992); 36 5959 (1995) (α -keto amide) JOC 52 3211 (1987) (β -hydroxy ketone); 56 741 (1991) (δ -hydroxy- β -keto ester); 58 2523 (1993) (δ -hydroxy- β -keto ester); 60 6866 (1995) JACS 110 3560 (1988) (β -hydroxy ketone); 112 1597, 2998 (1990) (both β -hydroxy ketones); 114 2260 (δ -hydroxy- β -keto ester), 9434 (β -hydroxy ketone) (1992); 115 1608, 4497 (β -keto ester) (1993) SL 448 (1990) (β -keto thioester)
$(n\text{-Bu}_4\text{N})\text{HB}(\text{OAc})_3$	TL 24 4287 (1983) (aldehydes only)
LiHBEt_3	JOC 45 1 (1980); 52 5700 (1987) JACS 108 3385 (1986) TL 27 6233 (1986); 30 5447 (1989)
KHBEt_3	TL 26 4643 (1985) (β -keto amides) Bull Korean Chem Soc 8 285 (1987)

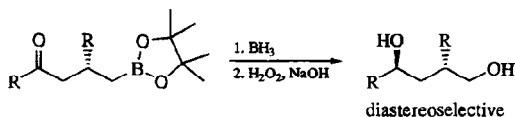
- LiHB(*sec*-Bu)₃ (L-Selectride) JACS 94 7159 (1972); 95 4100 (1973); 110 4475 (1988); 111 1396 (1989) (stereochemistry)
TL 141 (1973); 4487 (1978); 28 35 (1987); 29 5767 (1988) (α -alkoxy ketone); 32 1335 (1991); 35 8541 (1994)
JOC 50 3957 (1985); 53 869 (1988) (γ -alkoxycarbonylamino- β -keto ester); 55 99 (1990); 58 4484 (1993)
- KHB(*sec*-Bu)₃ (K-Selectride) JACS 95 4100 (1973)
TL 4487 (1978); 28 2999 (1987); 32 1335 (1991)
CC 1239 (1982)
JOC 53 3057 (1988)
Bull Korean Chem Soc 10 382 (1989)
- LiHB(Sia)₃ JACS 98 3383 (1976)
TL 4487 (1978)
- KHB(Sia)₃ JOC 51 238 (1986)
- $K \left[\begin{array}{c} H \\ R \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} B \right]$ TL 29 1069 (1988)
- $Li^+ \left[\begin{array}{c} \diagup \\ \diagdown \end{array} B \right]$ JACS 92 709 (1970)
JOC 52 4898 (1987)
- Li or KHB(Et)[C₆H₂(*i*-Pr)₃-2,4,6]₂ TL 32 6243 (1991)
- KHBPh₃ JOC 51 226 (1986); 52 5564 (1987)
- Li(*n*-Bu)₂B  JACS 98 1965 (1976)
- (*n*-Bu₄N)B₃H₈ TL 23 3337 (1982)
- i*-Bu₂Al-O--CH₃, *i*-Bu₂AlH JACS 109 7488 (1987) (β -keto ester)
- (HAlN-*i*-Pr)₆ TL 2369 (1977)
Z Chem 17 18 (1977)
- AlH₃ JACS 88 1464 (1966); 90 2927 (1968)
JCS B 581 (1967)
- AlH₃·NEt₃ JOC 58 3974 (1993)
- i*-Bu₂AlH Ann 623 9 (1959)
JOC 24 627 (1969); 47 2590 (1982); 50 2443 (1985); 55 2120 (1990) (α -sulfoxide)
CC 213 (1970)
Syn 617 (1975) (review); 732 (1982)
JACS 107 2730, 7524 (1985); 112 866 (1990) (δ -hydroxy- β -keto imide); 115 10139 (1993) (β -hydroxy ketone)
Ber 118 722 (1985) (β -diketone to 1,3-diol)

- TL 26 435 (1985) (α -sulfoxide); 27 3009 (β -hydroxy ketone), 6233 (1986); 28 4861, 4865 (1987) (both α -sulfoxide); 32 2219, 2223 (1991); 33 1605 (β,δ -diketo sulfoxides to 3-hydroxy-4-sulfinyl-1-alkanone), 2477 (γ -sulfinyl- β -keto ester), 7525 (β,δ -diketo esters to 3,5-dihydroxyalkanoate esters) (1992); 34 363 (α -sulfoxide), 513 (β,δ -diketo ester to β -hydroxy- δ -keto ester) (1993); 35 1785, 1937 (both α -sulfoxides), 5263 (β -hydroxy ketone), 5297 (α -sulfoxide), 8541 (1994)
- SL 460 (1990); 449 (1992) (both α -sulfoxide)
- i*-Bu₂AlH, MgBr₂ TL 34 5483, 5487 (1993)
JOC 60 7870 (1995)
- i*-Bu₂AlH, TiCl₄ JOC 59 705 (1994) (β -alkoxy ketone, β -keto ester)
- i*-Bu₂AlH, ZnCl₂ TL 26 435 (1985) (α -sulfoxide); 28 797 (α -sulfoxide), 4861 (α -sulfoxide), 6481 (β -hydroxy ketone) (1987); 31 6649, 6653 (1990) (both α -sulfoxide); 33 2477 (γ -sulfinyl- β -keto ester), 2733 (α -sulfoxide) (1992); 34 363 (1993) (α -sulfoxide); 36 4559 (1995) (α -sulfoxide)
JOC 52 304 (1987); 55 2120 (1990) (α -sulfoxide); 56 3083 (1991) (γ -keto acid); 57 1219 (1992) (β -amido)
SL 460 (1990); 167 (1992) (both α -sulfoxide)
- i*-Bu₂AlH, ZnBr₂ TL 35 1785, 1937, 5297 (1994) (all α -sulfoxides)
- i*-Bu₂AlH/NaBH₄, Et₂BOMe JOC 56 5752 (1991) (β,δ -diketo ester to 3,5-dihydroxyalkanoate esters)
- i*-Bu₃Al Ann 623 9 (1959)
- i*-Bu₃Al, amine BCSJ 51 2664 (1978)
- LiAlH₄ JACS 69 1196 (1947); 71 1675 (1949); 78 2579 (1956); 88 1458 (1966); 98 8114 (1976); 110 4475 (1988)
Org Rxs 6 469 (1951)
JCS C 968 (1969)
Tetr 26 2411 (1970); 35 449, 567 (1979)
JOC 43 2173 (1978); 44 2760 (1979); 52 1425 (β -diketones to 1,3-diols), 4062 (β -hydroxy ketones) (1987); 55 2120 (1990) (α -sulfoxide)
TL 4487 (1978); 26 435 (1985) (α -sulfoxide); 29 1021 (1988) (β -silyloxy); 33 1759 (1992); 35 5263 (β -hydroxy ketone), 9513 (1994)
Ber 118 704 (1,2-, 1,3-, 1,4-, and 1,5-diketones to diols), 722 (1,2- and 1,3-diketones to diols) (1985)
- NaAlH₄ JOC 58 4727 (1993)
- LiAlH₄, silica gel TL 23 4585 (1982) (α,β,γ and δ -keto ester to hydroxy ester)

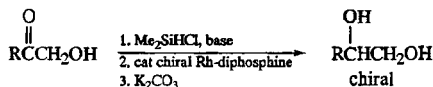
LiAlH_4 , py	JACS 84 1756 (1962)
LiAlH_4 , LiI	TL 29 5419 (β -alkoxy ketones), 5423 (β -hydroxy ketone) (1988); 30 4387 (1989) (β -hydroxy ketone)
LiAlH_4 , AlCl_3	JOC 30 3809 (1965)
LiAlH_4 , TiCl_4	JOC 52 1425 (1987) (β -diketones to 1,3-diols); 57 1219 (1992) (β -amido) SL 463 (1990) (β -amino ketone)
$\text{LiAl}(\text{OCH}_3)_3$	JACS 87 5614, 5620 (1965); 106 6414 (1984) Tetr 26 2411 (1970) Ber 118 722 (1985) (β -diketone to 1,3-diol)
$\text{LiAl}(\text{O}-i\text{-Bu})_3$	JACS 80 5372 (1958); 87 5620 (1965); 107 686, 2730 (1985); 111 4852 (1989) Coll Czech Chem Commun 24 2284 (1959) Tetr 24 2039 (1968); 26 2411 (1970) JOC 52 1425 (β -diketones to 1,3-diols), 1429, 4495 (1987); 53 5534 (1988) TL 28 1439, 3839 (1987); 35 8541 (1994)
$\text{LiAl}(\text{O}-i\text{-Bu})_3$, LiI	TL 30 4383, 4387 (1989) (both β -hydroxy ketones)
$\text{LiAl}(\text{O}-i\text{-Bu})_3$, TiCl_4	JOC 52 1425 (1987) (β -diketones to 1,3-diols)
$\text{LiAl}(\text{OCEt}_3)_3$	JOC 46 4628 (1981); 58 993 (1993) (chiral α -keto ester)
$\text{LiAl}(\text{OCEt}_2-i\text{-Bu})_3$	SL 585 (1993)
$\text{NaAlEt}_2 \left(\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \diagdown \quad \diagup \end{array} \right)$	JOC 58 1941 (1993)
$\text{LiAl}(i\text{-Bu})_2(i\text{-Bu})$	Syn 171 (1977) JOC 47 4581 (1982)
$\text{NaH}_2\text{AlEt}_2$	Bull Korean Chem Soc 13 199 (1992)
$\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$	TL 24 2653 (1983) (α -silyloxy ketones)
$\text{GaH}_3 \cdot \text{NR}_3$	TL 35 5915 (1994)
$\text{GaH}_3 \cdot \text{PCy}_3$	TL 35 5915 (1994)
LiInH_4	TL 36 3169 (1995)
LiH_3InPh	TL 36 3169 (1995)
$\text{LiH}_2\text{InPh}_2$	TL 36 3169 (1995)
Et_3SiH , $\text{CF}_3\text{CO}_2\text{H}$, NH_4F	SL 647 (1992)
Et_3SiH , HCl or H_2SO_4	JOC 39 2740 (1974)
Et_3SiH , BF_3	JOC 43 374 (1978)
Et_3SiH , $\text{BF}_3 \cdot \text{OEt}_2$	JOMC 117 129 (1976)
Et_3SiH , TiCl_4	TL 28 6331 (1987)

- PhMe₂SiH, cat *n*-Bu₄NF
JACS 106 4629 (1984)
JOC 51 2267 (1986) (mechanism); 52 3218 (1987)
(α -fluoro- β -keto ester); 53 5405 (1988)
- PhMe₂SiH, cat [(Et₂N)₃S]Me₃SiF₂
JACS 107 8294 (1985) (β -keto amides)
JOC 53 5405 (1988)
- PhMe₂SiH, CF₃CO₂H
JACS 107 8294 (1985) (β -keto amides)
JOC 53 5415 (1988) (α -alkoxy, acyloxy, amino,
alkoxycarbonylamino, arenesulfonylamino
ketones, β -keto ester, β -keto amides)
Org Syn Coll Vol 8 326 (1993) (β -keto amide)
- Ph₃SiH, AlCl₃
JOC 52 3218 (1987) (α -fluoro- β -keto ester)
- R₃SiH, cat TiCl₄
TL 29 6199 (1988)
- R₃SiH, cat ClRh(PPh₃)₃
TL 29 6199 (1988)
- R₂SiH₂ or R₃SiH (R = Et, Ph), cat RuCl₂(PPh₃)₃
JOC 47 2469 (1982)
- Ph₂SiH₂; KF, CsF, KO₂CH or (PhCH₂NMe₃)F
JOMC 172 143 (1979)
- PhSiH₃, cat *o*-Me₂NCH₂C₆H₄SnMe₂H, MeOH
JOC 58 3046 (1993)
- LiHSi 
JOC 52 948 (1987)
- LiHSi 
JOC 52 948 (1987)
- (MeO)₂SiMeH, cat *o*-Me₂NCH₂C₆H₄SnMe₂H,
MeOH
JOC 58 3046 (1993)
- (MeO)₃SiH, LiOMe
CC 1411 (1986)
TL 36 571 (1995) (α,β -epoxy ketone)
- (MeO)₃SiH, LiOCMe₂CMe₂OLi
CC 1411 (1986)
- (EtO)₃SiH, KF or CsF
CC 121 (1981)
Tetr 37 2165 (1981); 39 999 (1983)
- (EtO)₂SiMeH or Me₃SiO(SiHMeO)_{*n*}SiMe₃,
KF or KO₂CH
Syn 981 (1982)
- (MeHSiO)_{*n*}, *n*-Bu₂Sn(OAc)₂
JOC 38 162 (1973)
- n*-Bu₂SnH₂
JACS 83 1246 (1961)
- n*-Bu₂SnH₂, *p*-(NO₂)₂C₆H₄
TL 31 6381 (1990)
- Ph₂SnH₂
JACS 80 3798 (1958); 83 1246 (1961); 112
7001 (1990)
- R₂SnH₂ (R = *n*-Bu, Cy, Ph), TiCl₄
SL 965 (1995) (β -keto ester)
- n*-Bu₂SnFH
JOC 58 7608 (1993) (α,β -epoxy ketone)

$n\text{-Bu}_7\text{SnClH}$	JOC 57 4049 (1992); 59 4805 (1994) (both α -alkoxy ketones)
$n\text{-Bu}_3\text{SnH}$, pressure	JOC 51 1672 (1986)
$n\text{-Bu}_3\text{SnH}$, silica	JOC 43 3977 (1978); 59 7138 (1994) TL 35 883 (1994); 36 2757 (1995)
$n\text{-Bu}_3\text{SnH}$, $n\text{-Bu}_3\text{PO}$ or HMPT	CC 882 (1988) (α -chloro ketones)
$n\text{-Bu}_3\text{SnH}$, ZnCl_2	TL 27 3009 (1986) (β -hydroxy ketone)
$n\text{-Bu}_3\text{SnH}$, $n\text{-Bu}_4\text{NX}$ ($X = \text{F}, \text{Cl}$)	JOC 57 4049 (1992) (α -alkoxy ketones)
$n\text{-Bu}_3\text{SnH}$, $n\text{-Bu}_4\text{NCN}$	TL 35 8625 (1994) (α, β -epoxy ketone)
$o\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{SnMe}_2\text{H}$, MeOH	JOC 58 3046 (1993)
$o\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4\text{SnMe}_2\text{H}$, THF	JOC 58 3046 (1993) (β -hydroxy ketone)
Ph_3SnH	JOC 50 2149 (1985)
R_3SnH ($\text{R} = \text{Me}, n\text{-Bu}, \text{Ph}$), TiCl_4	SL 965 (1995) (β -keto ester)
cat Cp_2ZrH_2 , $i\text{-PrOH}$	JOC 51 240 (1986) (ketones only)
$[(\text{Ph}_3\text{P})_2\text{N}]\text{HM}(\text{CO})_4\text{L}$ ($\text{M} = \text{Cr}, \text{W}$; $\text{L} = \text{CO}$, $\text{P}(\text{OMe})_3$)/ $\text{CH}_3\text{CO}_2\text{H}$ or $\text{C}_6\text{H}_5\text{OH}$	JACS 107 2428 (1985)
$\text{HFe}(\text{CO})_4^-$, $\text{CF}_3\text{CO}_2\text{H}$	TL 29 5083 (1988)
$\text{KHF}(\text{CO})_4$	TL 35 8801 (1994) (PhCOCF_3 ; 1,2-diketones to 2-hydroxy-1-alkanone; α -keto ester or amide)
$\text{KHF}(\text{CO})_3[\text{P}(\text{OMe})_3]$	TL 35 8801 (1994) (PhCOCF_3)
LaNi_5H_6	CC 163 (1984) JOC 52 5695 (1987)
$\text{Li}_n\text{CuH}_{n+1}$ ($n = 1\text{--}5$)	JOC 43 183 (1978)



JACS 114 2759 (1992); 115 7517 (1993)



TL 33 2099 (1992)

2.4. Miscellaneous Reagents

electrolysis

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 1.5, p 129 (review)
JOC 59 1407 (1994)



- hydride delivery from carbon "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 1.3, p 79 (review)
- t*-BuMgCl, MAD TL 26 3853 (1985) (equatorial cyclohexanols)
JACS 110 3588 (1988)
- RMgX, cat Cp₂TiCl₂ TL 21 2171 (1980)
- i*-PrMgBr, (neomenthyl-Cp)₂TiCl₂ TL 29 4113 (1988)
- SmI₂, H₂O, THF JACS 109 6187 (1987); 110 4475 (1988)
JOC 58 5008 (1993)
TL 36 1661 (1995)
- SmI₂, ROH JACS 102 2693 (1980); 112 7001 (1990)
- LiO-*i*-Pr JCS C 804 (1969)
- cat LiO-*i*-Pr, cat NiCl₂, *i*-PrOH JOC 50 3082 (1985)
- Al(O-*i*-Pr)₃, *i*-PrOH Org Rxs 2 178 (1944) (review)
JACS 73 5824 (1951); 78 2579 (1956); 114 5018 (1992)
JOC 56 378 (1991)
- Al(O-*i*-Pr)₃, *i*-PrOH, CF₃CO₂H TL 36 3571, 5085 (1995)
- Al(OCHEt₂)₃, Et₂CHOH JACS 73 5824 (1951)
- Al[OCH(*i*-Pr)₂]₃, *i*-Pr₂CHOH JACS 73 5824 (1951)
- Al[OCH(*t*-Bu)₂]₃, *t*-Bu₂CHOH JACS 73 5824 (1951)
-
- JOC 44 1363 (1979); 60 16 (1994)
JACS 108 284 (1986)
Tetr 46 6633 (1990); 50 6819 (1994)
- R₂CHOH, cat chloroaluminum porphyrins (enantioselective) JOC 55 816 (1990)
- cat IrCl₄, HCl, cat P(OMe)₃, H₂O, *i*-PrOH Org Syn Coll Vol 6 215 (1988)
- cat Ln(O-*i*-Pr)₃ (Ln = La, Sm), *i*-PrOH TL 32 2355 (1991)
- amine, hν JACS 90 165 (1968); 91 3690 (1969); 102 5701 (1980); 103 1048, 6403 (1981);
114 1812 (1992)
Chem Rev 73 141 (1973) (review)
Top Curr Chem 66 1 (1976) (review)
- LDA JOC 43 2601 (1978)
TL 3945 (1979); 29 4057 (1988) (aldehydes)
- (*i*-Pr₂N)₂Mg TL 29 139 (1988)
- Ph₂SbH, AlCl₃ or TiCl₄ TL 26 5171 (1985)
- Na₂S₂O₄, H₂O, DMF TL 22 179 (1981)
- H₂Se, hν Angew Int 19 1008 (1980)

Na_2Te	JOC 58 241 (1993) (aryl aldehydes and ketones only)
$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, Na_2CO_3 , cat Pd-C, H_2O	JOC 50 3408 (1985) (aryl aldehydes only)
$(\text{Et}_3\text{NH})\text{H}_2\text{PO}_2 \cdot 1.5\text{H}_2\text{O}$, cat $\text{RuCl}_2(\text{PPh}_3)_3$	JOC 54 949 (1989)
NaO_2CH , KH_2PO_4 , 1-methyl-2-pyrrolidinone	JOC 46 3367 (1981)
HCO_2H , cat $\text{RuCl}_2(\text{PPh}_3)_3$	BCSJ 55 2441 (1982)
enzymes	"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 1.8, p 183 (review)



JACS 112 6447 (1990); 115 7906 (1993)

2.5. Reduction of Aldehydes in Preference to Ketones

H_2 , cat $\text{RuCl}_2(\text{PPh}_3)_3$	CL 1085 (1977)
H_2 , cat $\text{H}_3\text{Ir}(\text{PPh}_3)_3$, HOAc	JOMC 129 C43 (1977)
HCO_2H , Et_3N , cat $\text{RuCl}_2(\text{PPh}_3)_3$	TL 26 3365 (1985)
BH_3	J Korean Chem Soc 22 259 (1978)
BH_3 , LiCl	J Korean Chem Soc 22 259 (1978)
$\text{BH}_3 \cdot t\text{-BuNH}_2$	TL 21 697 (1980) JOC 51 4047 (1986)
$\text{BH}_3 \cdot \text{Me}_2\text{N}-\text{C}_5\text{H}_4\text{N}$	Bull Korean Chem Soc 9 188 (1988)
$\text{BH}_3 \cdot \text{py}$, cat HOAc	JOC 59 523 (1994)
9-BBN \cdot py	JOC 42 4169 (1977)
 , cat $\text{BF}_3 \cdot \text{OEt}_2$	TL 25 2985 (1984)
CB	JOC 42 512 (1977)
SiaB 	JOC 43 1470 (1978)
$(\text{Ipc})_2\text{BCl}$	SL 331 (1995)
$(\text{Ipc})_2\text{BOH}$	Org Prep Proc Int 27 541 (1995)
BH_4 exchange resin	TL 24 5367 (1983)
LiBH_4	Austral J Chem 28 1383 (1975) J Korean Chem Soc 22 259 (1978)
LiBH_4 , molecular sieves	JOC 44 3969 (1979)
NaBH_4	Austral J Chem 28 1383 (1975) Syn Commun 18 1927 (1988)

NaBH ₄ , <i>n</i> -Bu ₄ NBr, H ₂ O, C ₆ H ₆	Ind J Chem B 25 626 (1986)
NaBH ₄ , <i>t</i> -BuSH	TL 263 (1977)
NaBH ₄ , NiCl ₂ /Me ₃ SiCl	TL 28 5741 (1987)
NaBH ₄ , ErCl ₃ , aq EtOH	TL 22 4077 (1981)
(Et ₄ N)BH ₄	TL 21 3963 (1980)
(Ph ₃ P) ₂ CuBH ₄ , HCl	TL 22 675 (1981)
Zn(BH ₄) ₂	TL 31 7663 (1990) SL 885 (1993) (review)
Zn(BH ₄) ₂ -polyvinylpyridine	Syn Commun 21 2275 (1991)
(<i>n</i> -Bu ₄ N)BH ₃ CN	JACS 95 6131 (1973)
NaHB(OAc) ₃	CC 535 (1975)
KHB(OAc) ₃	TL 4851 (1979)
(<i>n</i> -Bu ₄ N)HB(OAc) ₃	TL 24 4287 (1983)
NaHB(OC ₆ H ₃ R ₂ -3,5) ₃ (R = Me, <i>t</i> -Bu)	CL 461 (1981)
KHBPh ₃	JOC 51 226 (1986)
Li{ <i>n</i> -Bu ₂ B \bigcirc }	JACS 98 1965 (1976)
<i>i</i> -Bu ₂ AlCl	SL 1055 (1995)
LiAl(O- <i>t</i> -Bu) ₃	Austral J Chem 28 1383 (1975) JACS 108 4586 (1986)
LiAl(OCEt ₃) ₃	JOC 46 4628 (1981)
(MeO) ₃ SiH, LiOMe	CC 1411 (1986)
(EtO) ₃ SiH, KF or CsF	CC 121 (1981) Tetr 37 2165 (1981); 39 999 (1983)
(EtO) ₂ SiMeH or Me ₃ SiO(MeSiHO) _n SiMe ₃ , KO ₂ CH	Syn 981 (1982)
<i>n</i> -Bu ₃ SnH, silica	JOC 43 3977 (1978)
EtCH(OMgBr) ₂	TL 22 621 (1981)
SmI ₂ , MeOH	Nouv J Chim 1 5 (1977) JACS 102 2693 (1980)
<i>i</i> -PrOH, cat Cp ₂ ZrH ₂	JOC 53 3752 (1988)
<i>i</i> -PrOH, cat Cp ₂ HfH ₂	JOC 53 3752 (1988)
<i>i</i> -PrOH or (<i>i</i> -Pr) ₂ CHOH, alumina	TL 3601 (1975) JOC 42 1202 (1977)

2.6. Reduction of Ketones in Preference to Aldehydes

NaBH ₄ , MCl ₃ ·6H ₂ O (M = Ce, Er, Cr, La), EtOH	JACS 101 5848 (1979) JOC 44 4187 (1979) TL 22 4077 (1981)
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- $t\text{-BuNH}_2 / \text{LiAl}(\text{O}-t\text{-Bu})_3 / \text{H}_3\text{O}^+$ or alumina TL 21 5085 (1980)
 Tetr 38 1827 (1982)
- $\text{Ti}(\text{NEt}_2)_4 / \text{LiAlH}_4 / \text{H}_2\text{O}$ CC 406 (1983)

2.7. Selective Reduction Between Aldehydes

- BH_4 exchange resin TL 24 5367 (1983)
- $i\text{-Bu}_2\text{AlCl}$ SL 1055 (1995)

2.8. Reduction of Conjugated Aldehydes in Preference to Nonconjugated Aldehydes

- $\text{NaBH}_4, \text{ErCl}_3$ TL 22 4077 (1981)

2.9. Reduction of Conjugated Aldehydes in Preference to Enones

- $\text{Zn}(\text{BH}_4)_4$ JOC 55 5799 (1990)
 SL 885 (1993) (review)

2.10. Selective Reduction Between Ketones

- BH_3 J Korean Chem Soc 22 259 (1978)
- BH_3, LiCl J Korean Chem Soc 22 259 (1978)
- $\text{BH}_3 \cdot t\text{-BuNH}_2$ TL 21 697 (1980)
- $(\text{Ipc})_2\text{BCl}$ SL 331 (1995)
- KHBPh_3 JOC 51 226 (1986)
- $\text{Li}[\eta\text{-Bu}_2\text{B} \langle \text{Cyclohexadiene} \rangle]$ JACS 98 1965 (1976)
- LiBH_4 J Korean Chem Soc 22 259 (1978)
- NaBH_4 JACS 74 2814 (1952)
- $\text{NaBH}_4, \text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ JOC 44 4187 (1979)
- BH_4 exchange resin TL 24 5367 (1983)
- $i\text{-Bu}_2\text{AlCl}$ SL 1055 (1995)
- $\text{MAD} / t\text{-BuMgCl}$ TL 26 3853 (1983) (cyclic > acyclic)
- $\text{MAD} / i\text{-Bu}_2\text{AlH}$ JACS 110 2650 (1988) (more hindered ketone reduced)
- $$\text{Al} \left[\begin{array}{c} t\text{-Bu} \\ | \\ \text{O} - \text{C}_6\text{H}_3 - \text{Mc} \\ | \\ t\text{-Bu} \end{array} \right]_3 / i\text{-Bu}_2\text{AlH}$$
 SL 719 (1995)
- $\text{Al}(\text{Hg}), \text{H}_2\text{O}, \text{THF}$ TL 29 525 (1988)

2.11. Reduction of Enones in Preference to Aldehydes

- $\text{NaBH}_4, \text{CeCl}_3, \text{EtOH}$ JOC 47 381 (1982)

2.12. Reduction of Enones in Preference to Ketones

NaBH ₄ , CeCl ₃	JOC 44 4187 (1979)
NaBH ₃ CN	JOC 47 2553 (1982)
(HAIN- <i>i</i> -Pr) ₆	TL 2369 (1977)

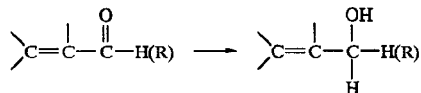
2.13. Reduction of Ketones in Preference to Enones

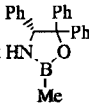

BH ₃ ·SMe ₂	TL 22 4929 (1981)
BH ₃ ·NH ₃	TL 21 693 (1980)
BH ₃ · <i>t</i> -BuNH ₂	IACS 111 278 (1989)
NaBH ₄	JCS 3426 (1955); 2680 (1960) TL 21 693 (1980); 27 4461 (1986); 29 517 (1988)
Zn(BH ₄) ₂	JOC 55 5799 (1990) SL 885 (1993) (review)
LiHAl(O- <i>t</i> -Bu) ₃	Tetr 24 2039 (1968)
<i>i</i> -PrOH, cat Cp ₂ HfH ₂	JOC 53 3752 (1988)

2.14. Reduction of Enals and Enones to Allylic Alcohols

For enone to saturated ketone reductions, see page 13, Section 3.6.

For stereochemistry of various reagents, see TL 34 6745 (1993)



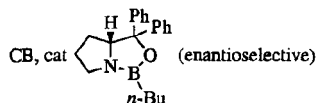
H ₂ , cat Pt-Ge	CC 1729 (1986)
H ₂ , cat [H ₂ Ir(Et ₂ PPh) ₄] ⁺	CC 746 (1986)
LiH, VCl ₃	JOC 45 1041 (1980)
NaH, NaO- <i>t</i> -Am, ZnCl ₂	JOC 44 2203 (1979)
NaH, ZnCl ₂ , MgBr ₂	JOC 44 2203 (1979)
Mg, CdCl ₂ , H ₂ O	TL 34 1681 (1993)
BH ₃ ·SMe ₂	JOC 43 1829 (1978) Org Prep Proc Int 13 225 (1981) (review)
BH ₃ ·SMe ₂ , cat HN-  (enantioselective)	TL 36 3425 (1995)
BH ₃ · <i>t</i> -BuNH ₂	TL 21 693 (1980)
 NBH ₂	Syn 214 (1981)

9-BBN

JOC 40 1864 (1975); 41 1778 (1976); 42 1197 (1977)

TL 23 3405 (1982)

JACS 108 4561 (1986)



JOC 57 3846 (1992)

Ipc-9-BBN (enantioselective)

JOC 50 1384 (1985)

TL 34 3123 (1993)

LiBH₄

TL 34 3123 (1993)

LiBH₄, N,N'-dibenzoylcystine, t-BuOH
(enantioselective)

CC 413 (1984)

LiBH₄, TbCl₃

TL 27 4759 (1986)

NaBH₄

JOC 35 1041 (1970); 52 5560 (1987); 54 5629 (1989)

TL 2441 (1976); 28 5945 (1987)

NaBH₄, HOAc

JOC 54 5629 (1989)

NaBH₄, CeCl₃

CC 601 (1978)

JACS 100 2226 (1978); 101 5848 (1979); 103 5454 (1981); 104 1750 (1984); 107 268, 1763, 5219 (1985); 108 2090, 3110, 3731, 3739 (1986); 109 2082, 3017, 3025, 3987, 4690, 6199, 8119 (1987); 116 7658 (1994)

JOC 44 689, 4187 (1979); 47 381, 1855 (1982); 49 2152 (1984); 50 2981 (1985); 51 491, 789, 1622 (1986); 52 943, 3250, 3541, 4135, 5233, 5457, 5624 (1987); 56 6538 (1991); 57 3173, 3365, 3846 (1992); 58 1501 (1993); 59 1396 (1994)

Syn Commun 12 167 (1982)

TL 27 6341 (1986); 28 333, 4951, 5655, 5977, 6253, 6485 (1987); 30 601 (1989); 34 3123 (1993); 36 2321 (1995)

NaBH₄, EuCl₃

JACS 111 7525 (1989)

NaBH₄, PrCl₃·6H₂O, tartaric acid

JACS 112 8985 (1990)

Zn(BH₄)₂

JACS 109 3981 (1987)

Zn(BH₄)₂-silica gel

JOC 56 4796 (1991)

(n-Bu₄N)BH₄

TL 34 3123 (1993)

(PhCH₂NEt₃)BH₄, (i-PrO)₂TiCl₂

JOC 58 5981 (1993)

NaBH₃CN, H⁺, MeOH


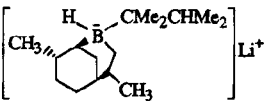
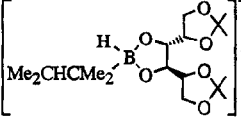

JOC 40 2530 (1975)

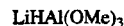
NaBH₃CN, CF₃CO₂H

JOC 45 216 (1980)

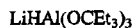
(n-Bu₄N)BH₃CN, H⁺, MeOH

JOC 40 2530 (1975)

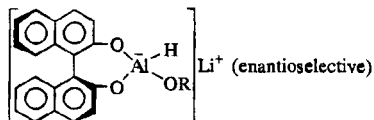
LiH_3BN 	TL 34 257 (1993) JOC 59 6378 (1994)
$\text{LiH}_3\text{B}(n\text{-Bu})$	JOC 47 3311 (1982)
LiHBEt_3	JOC 52 4665 (1987) TL 34 3123 (1993)
$\text{LiHB}(\text{sec-Bu})_3$	TL 4487 (1978); 34 2745, 3123 (1993) CC 1226 (1987)
$\text{LiHB}(\text{Sia})_3$	TL 4487 (1978)
$\text{KHB}(\text{sec-Bu})_3$	TL 4487 (1978) JOC 53 3057 (1988)
KHBPh_3	JOC 52 5564 (1987)
	JACS 94 8616 (1972)
	JOC 52 4020 (1987) (K^+ (enantioselective))
NaH_3BOAc	JOC 54 5629 (1989)
$\text{NaHB}(\text{OAc})_3$	TL 28 5755 (1987) JOC 54 5629 (1989)
$\text{NaHB}(\text{OMe})_3$	JACS 110 1985 (1988)
LiAlH_4	JCS 5280 (1965) JOC 34 2206 (1969); 35 1041 (1970) Org Syn Coll Vol 6 769 (1988) TL 34 2745 (1993)
LiAlH_4 , LiBr or MgBr_2	TL 28 5681 (1987)
LiAlH_4 , AlCl_3	JOC 35 2971 (1970)
LiAlH_4 , $\text{ArNHCH}_2\text{CH}(\text{NHCH}_3)\text{CH}_2\text{CH}_2\text{OH}$ (Ar = Ph; 2,6- $\text{Me}_2\text{C}_6\text{H}_3$) (enantioselective)	TL 24 4123 (1983)
LiAlH_4 , PhCHOHCHMeNMe_2 ,  (R = Me, Et, <i>i</i> -Pr, PhCH_2 ; enantioselective)	CL 239 (1984)
LiAlH_4 , PhCHOHCHMeNMe_2 , EtNHPH (enantioselective)	CC 1026 (1980)
LiAlH_4 , $\text{PhCH}_2\text{COHPhCHMeCH}_2\text{NMe}_2$ (Darvon alcohol, enantioselective)	TL 27 4759 (1986)
$\text{LiHAl}(\text{i-Bu})_2(n\text{-Bu})$	JACS 102 7910 (1980) JOC 49 1717 (1984); 58 11 (1993)



JOC 34 2206 (1969)



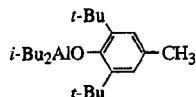
TL 34 2745 (1993)

JACS 106 6717 (1984); 110 4718 (1988)
CC 1226 (1987)JOC 34 2206 (1969); 35 2971 (1970); 38
1380 (1973)
TL 28 503 (1987)CC 213 (1970)
JACS 102 7910 (1980); 109 3017, 3025, 3981
(1987); 111 5312 (1989)
JOC 50 2443 (1985); 51 5232 (1986); 52 1907, 3841
(1987)

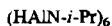
TL 28 61 (1987)



JOC 47 4640 (1982)

JOC 44 1363 (1979)
BCSJ 54 3033 (1981)
JACS 106 3875 (1984)
Ann 321 (1987)
TL 34 3123 (1993)

BCSJ 54 3033 (1981)



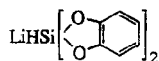
TL 2369 (1977)



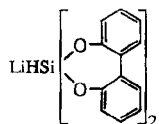
TL 35 5915 (1994)



JACS 106 4629 (1984)



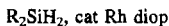
JOC 52 948 (1987)



JOC 52 948 (1987)



Organomet 1 1390 (1982)



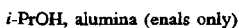
JOC 53 3057 (1988)

Bull Acad Sci USSR, Div Chem Sci 26
995 (1977)

JACS 80 3798 (1958)



JOC 43 183 (1978)



TL 3601 (1975)

i-PrOH or cyclopentanol, cat [Ir(COD)OMe]₂
plus *n*-PrN(CH₂CH₂PPh₂)₂ or
Et₂NCH₂CH₂N(CH₂CH₂PPh₂)₂

JACS 112 9190 (1990)

i-PrOH, MgO

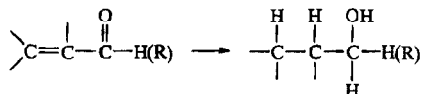
TL 30 2705 (1989)

baker's yeast (enantioselective)

CL 587 (1984)

TL 36 123 (1995)

2.15. Reduction of Enals and Enones to Saturated Alcohols



baker's yeast (enantioselective)

CC 846 (1975); 999 (1979); 205 (1982)

Helv 59 1832 (1976)

CL 587 (1984); 1395 (1985)

JOC 50 4625 (1985); 57 2052 (1992)

TL 27 4737 (1986); 31 4195 (1990)

JCS Perkin I 1743 (1987); 3061 (1988)

H₂, cat [Rh(COD)(*i*-Pr₂PC₅H₄FeC₅H₄P-*i*-Pr₂)]OTf

TL 35 4963 (1994)

H₂, cat Rh-alumina

TL 28 5615 (1987)

H₂, Raney nickel T-4

JOC 53 1574 (1988)

H₂, NaH-*t*-AmOH-Ni(OAc)₂

JOC 45 1937 (1980)

Li, NH₃/Li, MeOH/NH₄Cl

JACS 108 800 (1986)

Li, NH₃, EtOH

JACS 86 1761 (1964)

JOC 50 2981 (1985)

Li, NH₃, NH₄Cl

CC 1044 (1987)

Mg, MeOH

Ann 468 117 (1929)

NaBH₄, MeOH

Tetr 15 193 (1961)

JCS C 616 (1968)

JOC 35 2971 (1970)

JACS 108 3443 (1986)

NaBH₄, *i*-PrOH

Tetr 15 193 (1961)

JCS C 616 (1968)

JOC 35 1041 (1970)

NaBH₄, py

Tetr 15 193 (1961)

JCS 5280 (1965)

NaBH₄-exchange resin, CuSO₄, MeOH

Bull Korean Chem Soc 14 749 (1993)

KHB(*sec*-Bu)₃, EtOH

Austral J Chem 34 745 (1981)

JOC 58 2867 (1993)

KHBPh₃

JOC 52 5564 (1987)

LiAlH₄

TL 31 5303 (1990); 35 1137 (1994)

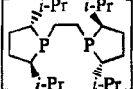
NaAlH ₄	JOC 58 4727 (1993)
NaH ₂ Al(OCH ₂ CH ₂ OCH ₃) ₂	TL 31 5303 (1990)
Et ₃ SiH, CF ₃ CO ₂ H	JOC USSR 7 2145 (1971)
HFe(CO) ₄ ⁻	BCSJ 55 1329 (1982)
LaNi ₅ H ₆	JOC 52 5695 (1987)
LaNi _{4.5} Al _{0.5} H ₅	JOC 52 5695 (1987)
[HCu(PPh ₃) ₃] ₆ , H ₂ O	TL 30 5677 (1989)

2.16. Asymmetric Reduction of Aldehydes and Ketones

Reviews:

Syn 329 (1978) (asymmetric hydrogenation and hydrosilylation)
 Tetr 37 3547 (1981) (organoboron reagents); 42 5157 (1986) (chiral metal hydride complexes)
 JACS 105 3725 (1983) (Cram and anti-Cram reduction of α -chiral ketones)
 "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Chpt 2 (chiral boron reagents), Chpt 3 (LiAlH₄ derived reagents)
 Topics Stereochem 14 231 (1983) (complex aluminum hydrides and tricoordinate aluminum reagents)
 JOC 52 5406 (1987) (reagent comparison)
 Chem Rev 89 1553 (1989) (organoboron reagents)
 Acct Chem Res 25 16 (1992) (organoboron reagents)
 Syn 605 (1992) (general)
 "Catalytic Asymmetric Synthesis," Ed. I. Ojima, VCH, New York (1993), Chpt 1 (hydrogenation)
 Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21d, G. Thieme, Stuttgart-New York (1995), pp 3945-4198 (general)

H ₂ , cat Ru(OAc) ₂ (BINAP)	TL 29 1555 (1988) (β -keto ester)
H ₂ , cat RuX ₂ (BINAP) (X = Cl, Br)	JACS 109 5856 (1987) (β -keto esters); 110 629 (many functionalized ketones), 6210 (β -keto ester) (1988); 111 9134 (1989) (β -keto ester); 112 5583 (1990) (β -keto ester); 113 6639 (1991) (β -keto ester); 115 144 (β -keto ester), 3360 (β -diketone to diol, β -keto ester) (1993); 116 1753 (1994) (β -keto ester) TL 29 1555, 6327 (1988) (both β -keto esters); 31 5509 (1990) (γ -keto esters); 35 3325, 4559 (1994) (both β -keto esters); 36 2063 (α -chloro- β -keto ester), 5769 (α -acetamido- β -keto phosphonate) (1995) SL 475 (1993) (β -keto ester)
H ₂ , cat [(arene)RuX(BINAP)]X (X = Cl, Br, I)	CC 1208 (1989) (β -keto ester, α -amino ketone) JACS 111 9134 (1989) (β -keto ester) Tetr Asym 1 1 (1990) (β -keto ester) TL 31 7185 (1990) (β -keto ester); 32 4163 (1991) (β -keto ester; α - and β -hydroxy ketone; ArCOR) JOC 58 7932 (1993) (β -keto ester); 59 3064 (1994) (α - and β -keto esters, α -amino ketones)

- H_2 , cat $[\text{RuCl}_2(\text{C}_6\text{H}_6)]_2$, cat BINAP, DMF
 H_2 , cat $[\text{Ru}_2\text{Cl}_4(\text{BINAP})_2]\text{NEt}_3$
 H_2 , cat $\text{RuCl}_2(\text{COD})$, cat BINAP, cat Et_3N
 H_2 , cat $\text{RuCl}_2(\text{BINAP})$, cat chiral diamine, cat KOH
 H_2 , cat RuBr_2 
 H_2 cat $\text{Ru}(\text{COD})(2\text{-methylallyl})$, chiral ligand
 H_2 , cat $\text{Ru}(\text{DIPAMP})(2\text{-methylallyl})_2$ or $\text{Ru}_2\text{X}_2(\text{DIPAMP})$
 H_2 , cat $[\text{RuX}(\text{p-cymene})(\text{bichep})]\text{X}$ ($\text{X} = \text{Cl}, \text{I}$) or $\text{Ru}(\text{OAc})_2(\text{bichep})$
 H_2 , cat $[\text{RuI}_2(\text{p-cymene})]_2$, cat $o\text{-Ph}_2\text{P-Ar-Ar-PPh}_2$
 H_2 , cat $\text{RuBr}_2(\text{Biphenyl})$
 H_2 , cat $[\text{Rh}(\text{COD})\text{Cl}]_2$, cat chiral diphosphine
 H_2 , cat $[\text{Rh}(\text{COD})\text{Cl}]_2$, cat chiral $\text{R}_2\text{PNR-C}_2\text{-OPR}_2$
 H_2 cat $[\text{Ir}(\text{BINAP})(\text{COD})]\text{BF}_4$ or cat $[\text{Ir}(\text{H}_8\text{-BINAP})(\text{COD})]\text{BF}_4$, cat $(o\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{PPh}$
 H_2 , Raney Ni, tartaric acid
 chiral RBeCl
- JACS 117 2931 (1995) (β -keto phosphonates)
 TL 32 4381, 7699 (3,5-dioxoalkanoate esters to 3,5-dihydroxyalkanoate esters) (1991)
 TL 32 4227 (1991)
 JOC 57 5990 (1992); 59 4862 (1994) (all β -keto esters)
 JACS 117 2675, 10417 (1995)
 JACS 117 4423 (1995) (β -keto esters)
 TL 36 2062 (α -chloro- β -keto ester), 4801 (β -keto ester) (1995)
 TL 33 5343 (1992)
 TL 34 2351 (1993) (α -keto esters and amides)
 SL 827 (1991)
 SL 475 (1993) (β -keto ester)
 CC 428 (1977) (α -keto esters)
 Org Syn 63 18 (1984) (α -keto lactones)
 CL 1603 (1984) (α -keto esters, amides and lactones)
 TL 27 4477 (1986) (α -keto lactone); 28 3675 (1987) (α -keto lactone); 29 4755 (1988) (α -keto lactone); 30 363, 367 (1989) (both α -amino ketone); 32 4745 (1991) (α -keto amide); 35 9363 (1994)
 JACS 112 5876 (1990) (α - and β -amino ketones); 116 4062 (1994)
 Org Syn Coll Vol 7 417 (1990) (α -keto lactone)
 SL 193 (α -amino ketone), 689 (β -amino ketone) (1991); 829 (1992) (γ -amino hydrochloride)
 TL 29 3675 (1987) (α -keto esters and amides); 31 4139 (1990) (α -keto lactone)
 SL 358 (1995) (α -keto lactone and amide, α -amino ketone hydrochloride)
 JACS 115 3318 (1993) (cycloalkanones)
 BCSJ 36 155 (1963) (β -keto ester); 53 3367 (1980) (β -diketone to diol); 55 2186 (1982) (β -keto ester); 56 1414 (1983) (β -keto ester)
 JOC 54 2383 (1989) (aryl ketone)

chiral R_2Be

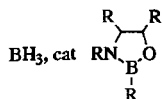
JOC 54 2383 (1989) (aryl ketone, ynone)

chiral $RMgX$

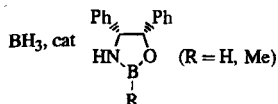
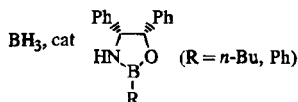
JOC 54 2383 (1989) (aryl ketone, ynone)

 BH_3 , cat chiral oxazaborolidines

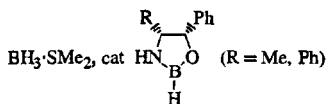
Tetr Asym 3 1475 (1992) (review)



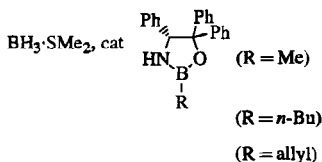
JACS 116 8516 (1994)

TL 34 4145 (1993); 36 4729 (1995)
(1,*n*-diones to diols; *n* = 2–6)

TL 34 4145 (1993)



SL 929 (1993)

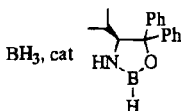


Tetr Asym 5 165 (1994)

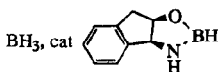
TL 36 3425 (1995) (enone)

Tetr Asym 4 15 (1993)

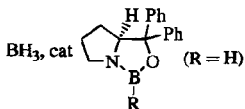
Tetr Asym 5 165 (1994)



JACS 109 5551 (1987)



TL 35 6631 (1994)



JACS 109 5551 (1987); 115 11028 (1993)

TL 29 3423 (1988) (enone)

JOC 53 2861 (1988)

(R = Me)

JACS 109 7925 (1987); 115 9842 (1993)

TL 29 3201, 6409 (1988); 30 5207 (1989); 32 2343,
6835, 7175 (1991); 34 785 (1993); 35 9375 (1994)

JOC 58 2880 (1993); 60 3205 (1995)


(R = Et)

TL 33 4141 (1992)


(R = <i>n</i> -Bu)	TL 31 611 (1990) (enones); 33 4141 (1992); 34 785 (1993); 35 6681 (1994) JACS 114 1906 (1992) (trichloromethyl ketones) JOC 57 7115 (1992)
(R = Ph)	TL 31 7415 (1990); 34 785 (1993) JOC 57 7115 (1992)
 BH ₃ , cat, <i>i</i> -PrOH	TL 35 6409 (1994) JOC 60 4324 (1995)
 BH ₃ , <i>i</i> -PrOH	TL 35 6409 (1994)
 BH ₃ , Et ₃ N	TL 34 3243 (1993)
 BH ₃ , cat (R ¹ = H, Me; R ² = β -naphthyl)	TL 30 6275 (1989)
 BH ₃ , cat (R = β -naphthyl) <i>n</i> -Bu	TL 31 601 (1990) JOC 56 442 (1991)
 BH ₃ , cat	TL 31 2341 (1990)
 BH ₃ , cat (various R and R')	JOC 56 763 (1991)
 BH ₃ , cat	TL 29 4453 (1988)
 BH ₃ , cat	TL 30 5547 (1989)
BH ₃ , various chiral β -amino alcohols	CC 315 (1981) (aryl ketones) JCS Perkin I 1673 (1983) (aryl ketones)

BH_3 , chiral $\text{RCH}(\text{NH}_2)\text{CPh}_2\text{OH}$

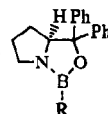
CC 469 (1983) (aryl ketones)
JOC 49 555 (1984) (aliphatic ketones); 52 5406
(1987) (review)
JCS Perkin I 2039 (aliphatic and aryl ketones;
 α -halo, α -OH, α -OSiMe₃, α -OAc ketones; α -keto
ester); 2615 (polymer-supported reagent, aryl
and α -halo ketones) (1985)
JACS 112 8985 (1990)

BH_3 , cat  CR_2OH ($\text{R} = \text{H}, \text{Ph}$)


JOC 58 4511 (1993)

BH_3 , cat  CR_2OH ($\text{R} = \text{H}, \text{Ph}$)

JOC 58 4511 (1993)

CB, cat  ($\text{R} = n\text{-Bu}$)
($\text{R} = i\text{-Bu}$)

TL 32 6835 (1991); 33 2319, 3431, 7103, 7107
(1992); 34 5227 (1993)
JOC 57 3846 (1992) (enone)
JACS 115 8873 (1993)

$\text{BH}_3 \cdot \text{SMe}_2$, cat  $\text{HOCPh}_2\text{CH}-\text{CHR}$ ($\text{R} = \text{H}, \text{Me}$)

TL 36 603 (1995)

$\text{BH}_3 \cdot \text{THF}$ or $\text{BH}_3 \cdot \text{SMe}_2$,
 $\text{MeSO}_2\text{NHCHMeCHPhOH}$

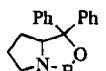
SL 429 (1995)

BH_3 , cat $\text{PhSO}(\text{NH})\text{CH}_2\text{CR}_2\text{OH}$

TL 34 6041 (1993)

$\text{BH}_3 \cdot \text{SMe}_2$; cat RNHPOPh_2 , $(\text{RNH})_2\text{POEt}$ or
 $(\text{RNH})_3\text{PO}$ ($\text{R} = \alpha\text{-phenethyl}$)

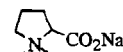
TL 34 7105 (1993)


 H_3B Me

TL 36 6957 (1995)

$\text{BH}_3 \cdot \text{py}$, cyclodextrin

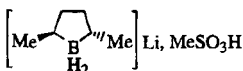
JOC 54 3482 (1989)


 H BH_3

Chem Pharm Bull 27 1479 (1979)

BH_3 , chiral Li amide

TL 27 635 (1986)

 Li , MeSO_3H

JACS 108 7402, 7404 (1986) (alkyl ketones)

lpcBH_2

JOC 49 2558 (1984) (low ee's)

$\text{lpcBH}(\text{O}-i\text{-Bu})$

JOC 49 3646 (1984) (low ee's)

lpcBRCI ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, t\text{-Bu}, \text{cyclopentyl},$
 $\text{CMe}_2\text{CHMe}_2$)

JOC 54 1577, 4504 ($\text{R} = t\text{-Bu}$) (1989)

(Ipc)₂BH

JACS 83 3166 (1961)

Tetr 24 6365 (1968)

JOC 42 2996 (1977)

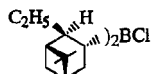
TL 35 1511 (1994)

(Ipc)₂BCl

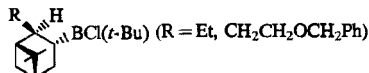
JOC 50 5446 (1985) (aryl ketones); 51 3394 (1986) (3° alkyl ketones); 52 5406 (1987) (review); 53 2916 (1988) (aryl ketones); 54 1191 (α-halo aryl ketone), 4504 (1989); 56 7076 (1991) (acyl silanes); 57 2379 (ynones), 7044 (aryl ketone), 7115 (aryl ketone) (1992); 58 62 (enone), 3731 (aryl ketone) (1993); 59 3055 (1994) (RCH=CHCOSiR₃); 60 41 (1995) (BrCH₂COCF₃)

JACS 110 1539 (1988) (aryl ketones, 3° alkyl ketones, α-keto esters); 115 9925 (1993) (aryl ketone)

TL 31 4677 (1990) (acyl silanes); 35 1511 (α-amino ketone), 2141 (ArCOMe) (1994); 36 3797 (1995) (Ar₂CO)



TL 32 6691 (1991)



JOC 54 4504 (1989)

Ipc-9-BBN (Alpine Borane)

JACS 99 5211 (1977) (1-deuteroaldehydes); 101 2352 (1979) (1-deuteroaldehydes); 102 867 (1980) (ynones); 106 1531 (α-keto esters), 3548 (ynone), 4192 (ynone), 7217 (1-deuteroaldehyde) (1984); 107 3915 (1985) (ynone); 110 5779 (1988) (1-deuteroaldehyde); 111 3382 (1-deuteroaldehyde), 8981 (1-tritioaldehyde) (1989); 112 297 (aldehyde to 1-deutero-1-alkanol), 4897 (1-deuteroaldehyde), 9652 (1-tritioaldehyde) (1990); 113 4704 (1991) (1-tritioaldehyde)

JOMC 156 203 (1978) (mechanism)

JOC 46 4107 (1981) (ynones); 47 1606 (alkyl ketones) (1982); 48 1784 (1983) (α-halo ketones); 49 1316 (1984) (alkyl ketones); 50 1384 (1985) (alkyl ketones, enones, ynones, α-halo ketones); 52 1372 (ynone), 2860 (ynone), 5406 (review) (1987); 53 1900 (1-deuteroaldehyde), 4282 (ynone) (1988); 54 159 (high pressure), 1161 (1-deuteroaldehyde) (1989); 56 2940 (1991) (1-tritioaldehyde); 57 1047 (1992) (ynone); 58 3516 (1993) (ynone); 59 4438 (1994) (aldehyde to 1-deutero-1-alkanol)

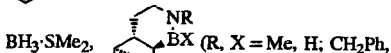
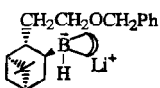
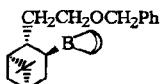
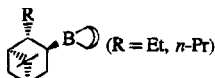
Tetr 40 1371 (1984) (ynones)

Org Syn 63 57 (1985) (ynone)

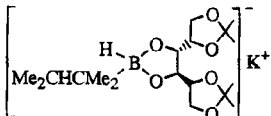
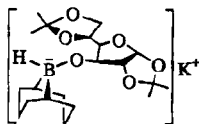
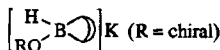
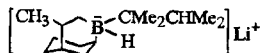
TL 29 423 (1988) (α-keto ester)

$[(\text{Ipc})_2\text{BHR}]\text{Li}$ ($\text{R} = \text{Me}, n\text{-Bu}$)

$(\text{IpcBH-9-BBN})\text{Li}$



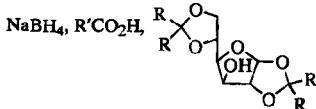
$\text{H}; n\text{-Pr}, \text{H}; n\text{-Pr}, \text{OMe}; n\text{-Pr}, \text{Me}$



LiBH_4 , N,N' -dibenzoylcystine, ROH

NaBH_4 , bovine serum albumin

NaBH_4 , hydroxymonosaccharide derivatives



Org Syn Coll Vol 7 402 (1990) (ynone)

SL 561 (1993) (aldehyde)

JCS C 2557 (1971)

JACS 93 1491 (1971)

JOC 42 2534 (1977)

TL 35 4891 (1994)

JOC 55 6328 (1990) (ynones, α -keto esters)

JOC 47 2814 (1982) (ynones); 55 6328 (1990)

Tetr 40 1371 (1984) (ynones)

JOC 47 2495 (1982); 52 5406 (1987); 56 1068 (1991)

JOC 57 2953 (1992)

JACS 93 1491 (1971)

JOC 51 3278 (1986)

JOC 51 1934 (RCOAr, hindered RCOR), 3278
(aliphatic and aryl ketones), 3396 (α -keto esters)
(1986); 52 5406 (1987) (review); 53 1231 (1988)
(aliphatic and aryl ketones, α -keto esters)

JOC 52 4020 (1987) (ketones, enones)

CC 413 (1984) (aryl ketones and enones); 138 (1985)
(3-aryl-3-oxo esters); 801 (1987) (acetylpyridines,
 α - and β -amino ketones)

TL 28 2837 (1987) (β -keto ester)

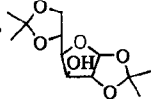
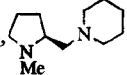
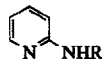
CC 926 (1978)

JOC 51 5423 (1986) (δ -keto acids)

JOC 44 1720 (1979)

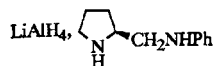
JOC 45 4229 [$\text{R}_2 = (\text{CH}_2)_5$], 4231 ($\text{R} = \text{Me}$) (1980)

JCS Perkin I 900 (1981) [$\text{R} = \text{Me}$; $\text{R}_2 = (\text{CH}_2)_5$]

- NaBH_4 , Me_3SiCl , cat $\text{PhSO}(\text{NH})\text{CH}_2\text{CPh}_2\text{OH}$ TL 34 8079 (1993)
- NaBH_4 , ZnCl_2 ,  CC 807 (1979)
 BCSJ 54 1424 (1981) (aryl ketones)
- $i\text{-Bu}_2\text{AlH}$, SnCl_2 ,  CL 2071 (1984); 813 (1985) (α -, β - and γ -keto esters)
 JOC 59 2700 (1994)
- $i\text{-Bu}_2\text{AlH}$, SnCl_2 , $\text{R}^1\text{N} \begin{array}{c} \text{R}^3 \\ | \\ \text{NR}^2 \end{array}$ TL 30 3551 (1989)
- LiAlH_4 , quinine Coll Czech Chem Commun 30 2487 (1965); 32 3897 (1967); 39 1869 (1974)
- LiAlH_4 , $(\text{Me}_2\text{NCH}_2\text{CHOH})_2$ Ber 107 1748 (1974); 113 1691 (1980)
- LiAlH_4 , PhCHOHCHMeNMe_2 , EtNHPH CL 981 (1980)
 CC 1026 (1980) (enones only)
 Chem Pharm Bull 31 837 (1983)
 TL 29 1461 (1988)
 JOC 59 2700 (1994)
- LiAlH_4 , PhCHOHCHMeNMe_2 ,  CL 239 (1984) (cyclic enones and aryl ketones)
 Chem Pharm Bull 33 52 (1985)
 TL 29 5661 (1988)
 JOC 53 4864 (1988); 55 4025 (1990); 57 3846 (1992)
- (R = Me, Et, Pr, *i*-Pr, PhCH₂)
- LiAlH_4 , PhCHOHCHMeNMe_2 , 2,5-Me₂C₆H₃OH Tetr 32 939 (1976)
 TL 2683 (1979); 21 1735, 1739 (1980); 24 4477 (1983) (all ynones)
 JOC 51 1264 (1986)
- LiAlH_4 , $\text{PhCHOHCHMeNMeCH}_2\text{-polymer}$, 2,5-Me₂C₆H₃OH JOC 51 3462 (1986)
- LiAlH_4 , $\text{PhCH}_2\text{COHPhCHMeCH}_2\text{NMe}_2$ (Darvon alcohol, Chiraid) JACS 94 9254 (1972); 99 8339, 8341 (1977); 107 1034 (1985) (4,6-alkadien-1-yn-3-one); 110 5904 (1988) (ynone); 111 3717 (1989) (ynone); 113 647, 1335 (1991)
 JOC 38 1870 (1973); 45 582 (1980) (ynone, aryl ketone); 55 2995, 5433 (ynone) (1990); 56 4913 (1991) (ynone); 57 1242, 2566 (1992) (both ynones)
 TL 27 4759 (1986) (enone); 30 1055 (1989); 31 7101 (1990)
- LiAlH_4 , $\text{ArNHCH}_2\text{CH}(\text{NHMe})\text{CH}_2\text{CH}_2\text{OH}$ TL 23 4111 (1982) (Ar = Ph); 24 4123 (1983) (Ar = Ph, 2,6-Me₂C₆H₃; enones)
- LiAlH_4 , PhCHMeNHMe-HCl TL 3195 (1973)
- LiAlH_4 , $\text{O}_2\text{S}(\text{NHCHMePh})_2$, MeNHPH JOC 49 3861 (1984)

LiAlH_4 , *o*- $\text{Me}_2\text{NC}_6\text{H}_4\text{CH}_2\text{NHCHMePh}$

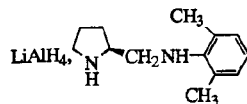
JOC 42 1578 (1977)



CL 783 (1977)

BCSJ 51 1869 (1978)

JOC 59 2700 (1994)



Heterocycles 12 (1979)

Tetr 37 4111 (1981)

JOC 59 2700 (1994)

LiAlH_4 , terpenic glycols

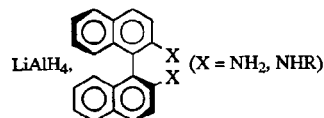
JOC 42 2073 (1977)

LiAlH_4 , *cis*-2,3-pinenediol

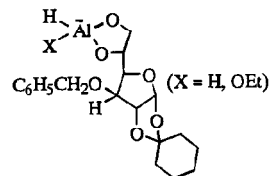
Ber 106 1312 (1973) (low ee's)

LiAlH_4 ; 1,4:3,6-dianhydro-D-mannitol or
1,3:4,6-di-*O*-benzylidene-D-mannitol

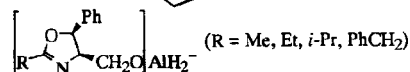
JCS Perkin I 1123 (1977) (very low ee's)



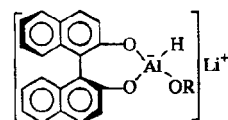
JOC 50 3013 (1985) (aryl ketones)



JCS C 1822, 2280 (1966); 197 (1967)



TL 1337 (1974)



JACS 101 3129, 5843 (1979); 106 6709, 6717 (1984)

(enones, ynones and aryl ketones); 108 6384

(1986); 113 647 (1991); 115 9305 (1993) (ynone)

Pure Appl Chem 53 2315 (1981) (review)

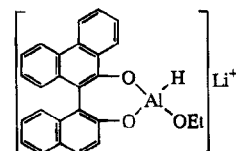
TL 22 247 (1981) (ynones); 29 1657 (1988) (1-

stannyl-2-alken-1-one); 30 5081 (1989)

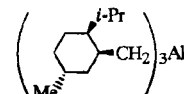
JOC 52 5406 (1987) (review); 53 5584 (1988) (acyl

stannanes); 56 893 (1991) (ArCOCF_3)

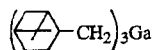
CC 1226 (1987)



CC 1490 (1984)



JOC 54 2383 (1989) (ynone)



(MeO)₃SiH, LiOCH₂CHROLi

(MeO)₃SiH, LiOCH₂CHRNHLi

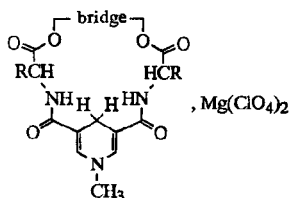
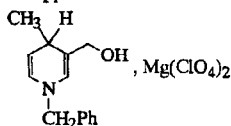
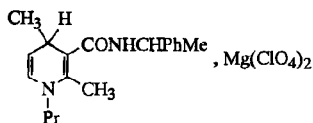
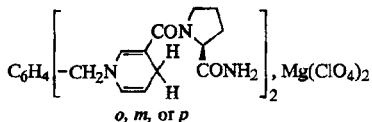
Me₃SiO(SiHMeO)_nSiMe₃, chiral titanocene catalyst / *n*-Bu₄F or HCl

R₂SiH₂ or R₃SiH, cat Rh(I), chiral ligand

Ph₂SiH₂, cat Rh-diop

Ph₂SiH₂, cat [RhCl(COD)]₂, cat chiral 1,10-phenanthroline / H₃O⁺

Ph₂SiH₂, cat [Rh(COD)₂]BF₄, cat chiral diphosphine / HCl or K₂CO₃, MeOH



chiral R₂CHOH, cat chloroaluminum porphyrins

i-PrOH, cat [RuCl₂(mesitylene)]₂, cat chiral TsNHCHPhCHPhNH₂, cat KOH

i-PrOH, cat RuX₂(diphosphine) (X = Br, 2-methylallyl), cat NaOH

i-PrOH, cat [RhCl(C₆H₁₀)]₂, cat chiral MeNHCHPhCHPhNHMe, cat KOH

TL 26 4949 (1985) (aryl ketones, ynones)

TL 29 89 (1988)

TL 29 89 (1988)

JACS 116 11667 (1994) (aryl ketones)

J Chem Res (S) 320 (1980)

CC 1238 (1982)

TL 30 5141 (1989)

CC 1238 (1982)

Tetr Asym 1 937 (1990)

TL 36 5239 (1995) (1,*n*-diones to diols; *n* = 2–5)

SL 347 (1995) (*n*-oxoalkanoate ester, *n* = 2–5)

JACS 103 4613 (1981)

JACS 101 7036 (1979) (α-keto esters, aryl ketones)

TL 29 5617 (1988) (aryl ketones, α-keto esters)

JACS 101 2759 (1979); 103 2091 (1981); 107 3981 (1985)

JOC 55 816 (1990)

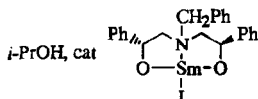
JACS 117 7562 (1995) (aryl ketones)

SL 478 (1993)

TL 34 6897 (1993)

i-PrOH, cat [RhCl(COD)]₂, cat chiral
1,10-phenanthroline, cat KOH

i-PrOH, cat Rh polymer, KOH



baker's yeast

Tetr Asym 1 635 (1990)

TL 36 8779 (1995)

JACS 115 9800 (1993) (aryl ketones)

Adv Carbohydr Chem 4 75 (1949) (review)

Org Syn Coll Vol 2 545 (1949) (α -hydroxy ketone); 7
215 (1990) (β -keto ester); 8 312 (1993) (β -
diketone to β -hydroxy ketone)

Can J Chem 29 678 (1951) (β -keto carboxylates)

Biochem 3 838 (1964) (ketones)

Biochem J 95 633 (1965) (5-oxodecanoic acid)

Coll Czech Chem Commun 31 2615 (1966) (methyl
ketones)

JACS 88 3595 (1966) (1-deuteroaldehydes); 102 870
(1980) (β -keto ester); 104 4251 (β -keto ester),
5473 (ketone) (1982); 105 5925 (1983) (β -keto
ester); 107 2993 (1985) (β -keto esters); 108 4912
(1986) (ketone); 109 8102 (1987) (β -keto ester);
110 6210 (1988) (β -keto ester)

CC 400 (1975) (α -hydroxy, halo and formyloxy
ketones; α -keto acid; α - and β -keto esters); 315
(1977) (α -PhSO, Cl, OAc ketones); 456 (1978)
(trifluoromethyl ketones); 908 (1979) (bicyclic
ketone); 599 (1983) (β -keto carboxylates); 138
(1986) (2,2-dithioalkan-1-ones); 1368 (1987) (β -
keto ester)

Austral J Chem 29 2459 (1976) (α - and β -keto esters
and amides); 31 1965 (1978) (α -RS, α -RSO, α -
RSO₂ ketones)

Helv 60 1175 (1977); 62 2829 (1979); 63 1383
(1980); 65 495 (1982); 66 485 (1983); 67 1843
(1984) (all β -keto esters)

BSCF II 215 (1978) (α -phosphate)

Tetr 37 1341 (1981); 41 919 (1985) (both β -keto
esters)

JOC 47 2820 (1982) (β -diketones to hydroxy
ketones); 50 127 (β -keto carboxylate), 3411 (β -
diketones to hydroxy ketones) (1985); 51 1253
(2,2-dithioalkan-1-ones), 2795 (α -fluoro ketones)
(1986); 52 192 (β -keto esters), 256, 1141, 1359 (β -
keto esters), 2036 (β -diketones to hydroxy
ketones), 2086 (α -acetoxo ketone), 2244 (β -keto
ester), 3223 (cyclic β -diketones to hydroxy
ketones), 4363 (γ - and δ -keto acids) (1987); 53
860, 1969, 2589 (α -keto ester), 4405 (α -acyloxy
ketone), 4962 (1988); 54 2238 (β -diketone to β -
hydroxy ketone), 2274, 3221 (α -diketone to α -
hydroxy ketone) (1989); 55 3917 (1990)

baker's yeast (*continued*)

(β -keto acids); 56 2237, 3619, 4778 (β -keto esters), 6019, 7177 (3-chloro-4-oxoalkanoate esters) (1991); 57 1047 (1992); 58 486 (3-chloro-2-oxoalkanoate ester), 2260 (3-oxoglutarates) (1993); 59 924, 3487 (α -keto lactone), 8288 (α -azido) (1994); 60 2022, 3546, 6198 (β -keto ester) (1995)

Angew Int 22 1012 (1983) (α -formyl ester)

Agric Biol Chem 47 1431 (1983) (γ - and δ -keto esters)

TL 24 2009 (1983) (β -keto ester); 25 1241 (β -diketones to β -hydroxy ketones), 4623 (3-oxo glutarate and adipate esters), 5083 (α -sulfenyl- β -keto esters) (1984); 26 101 (β -keto esters), 771 (α -PhS ketone), 4213 (β -keto esters) (1985); 27 565 (β -diketones to β -hydroxy ketones), 1915 (α -keto esters); 2091 (β -keto esters), 2657 (β -keto esters), 3547 (2-acyl-1,3-dithianes; 2-acylthiazoles), 4737 (α -chloro ketones), 4817 (α -PhSO₂ ketone), 5275 (β -keto esters and amides), 5281 (β -keto esters), 5397 (α -chloro ketone, β -keto ester), 5405 (β -keto thio- and dithioesters) (1986); 28 2709 (β -chloro- α -keto ester), 3189 (β -keto ester) (1987); 29 4769 (3- and 4-nitro ketones), 4865 (β -keto ester), 6167 (5-acetyl-2-isoxazolines) (1988); 30 2707 (β -keto ester), 3701, 5705 (β -keto ester) (1989); 31 1159 (β -keto ester), 1615 (β -keto ester), 1811, 3631 (β -keto esters), 4025 (α -hydroxy ketone), 4195 (2-acyl-2-alkenoate ester), 5575 (γ - and δ -keto sulfones), 7463 (β -diketone to β -hydroxy ketone) (1990); 32 399 (α -PhS ketone), 2643, 2927 (β -keto ester), 7055 (γ -keto ester), 7075 (α -keto ester) (1991); 33 2871 (α,γ -diketo ester to 2-hydroxy-4-oxoalkanoate ester), 5241, 5567 (β -diketone to β -hydroxy ketone), 5625 (α -keto lactone) (1992); 34 8271 (β -keto ester), 8453, 8481 (β -keto ester) (1993); 35 2845 (α -keto ester), 3937 (β -keto ester), 4985 (1994); 36 123 (enone), 3715 (β -keto ester) (1995)

Syn 897 (1983) (CH₃ and CF₃ ketones)

Chem Pharm Bull 31 4384 (1983)

(MeO₂CCOCHMeCO₂Me)

Org Syn 63 1 (1984) (β -keto esters)

CL 1475 (1985) (δ -keto acids)

SL 867 (1991) (3-chloro-4-oxoalkanoate ester); 837 (1995) (β -keto ester)

Chem Rev 91 49 (1991) (review)

Tetr Asym 4 1271 (1993) (α -halo, α -azido); 5 1727 (1994) (α -azido)

TL 31 267 (1990)

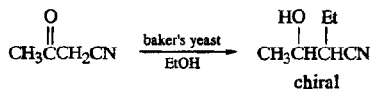
TL 30 2245 (1989) (β -keto ester)

baker's yeast, ClCH₂CO₂Et

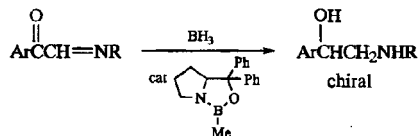
baker's yeast-magnesium alginate

baker's yeast, glucose, cat NADPH	TL 35 4569 (1994) (α -acetoxy)
alcohol dehydrogenase from baker's yeast and NADPH immobilized on Nucleosil 120-5 C ₁₈	TL 34 2359 (1993)
L-enzyme-1, NADPH	TL 36 591 (1995) (β -keto ester)
<i>Aspergillus niger</i>	JOC 53 5215 (1988) (β -diketones to β -hydroxy ketones) Tetr Asym 4 1271 (1993) (α -halo, α -azido); 5 1727 (1994)
<i>Beauveria sulfurescens</i>	JOC 54 3221 (1989) (α -diketone to diol); 59 8288 (1994) (α -azido) Tetr Asym 4 1271 (1993) (α -halo, α -azido); 5 1727 (1994) (α -azido)
<i>C. guilliermonde</i>	JACS 108 284 (1986)
<i>Candida albicans</i>	Chem Pharm Bull 31 4384 (1983) (MeO ₂ CCOCHMeCO ₂ Me)
<i>Candida parapsilosis</i>	JOC 55 4377 (1990) (α -diketones to α -hydroxy ketones, α -keto ester and amide)
<i>Corynebacterium equi</i> IFO 3730	JOC 52 2735 (1987) (α -PhS, α -PhSO and α -PhSO ₂ ketone)
<i>Cryptococcus macerans</i>	JOC 45 3352 (1980) (α -halo aryl ketones)
<i>Cunninghamella elegans</i>	Tetr Asym 5 1727 (1994) (α -azido)
<i>Dipodascus uninucleatus</i>	JACS 97 865 (1975)
<i>Geotrichum candidum</i>	TL 28 5037 (1987) (β -diketone to hydroxy ketone); 29 2453 (1988) (α - and β -keto ester); 34 6087 (1993) (β -keto ester); 35 147 (1994); 36 265 (1995) JOC 53 5215 (1988) (β -diketones to β -hydroxy ketones); 54 2238 (1989) (β -diketone to β -hydroxy ketone); 59 8288 (1994) (α -azido) Biocatalysis 5 249 (1992) (β -keto esters) Tetr Asym 4 1271 (1993) (α -halo); 5 1727 (1994) (α -azido)
<i>Kloeckera corticis</i> ATCC 20109	TL 23 5489 (1982) (2,2-dithio-1-alkanone)
<i>Lactobacillus kefir</i>	Tetr Asym 4 1271 (1993) (α -halo, α -azido); 5 1727 (1994) (α -azido) JOC 59 8288 (1994) (α -azido)
<i>Lactobacillus kefir</i> alcohol dehydrogenase, NADPH	JOC 57 1532 (1992)
<i>Mortierella isabellina</i>	Tetr Asym 4 1271 (1993) (α -halo, α -azido); 5 1727 (1994) (α -azido) JOC 59 8288 (1993) (α -azido)
<i>Mucor rammanianus</i>	JACS 97 865 (1975)
<i>Nicotiana tabacum</i>	JOC 54 4237 (1989) (β -keto esters)

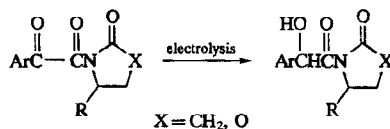
- Pseudomonas* sp. strain PED alcohol dehydrogenase JOC 57 1526 (1992)
- Rhizopus arrhizus* TL 36 6461 (1995) (α -cyano ketone)
- Rhodotorula glutinus* Tetr Asym 5 1727 (1994) (α -azido)
JOC 59 8288 (1994) (α -azido)
- Saccharomyces cerevisiae* (freeze-dried) TL 34 3949 (1993) (β -keto ester)
- Sporobolomyces pararoseus* JOC 43 2357 (1978) (aryl ketones)
- Sporotrichum exile* Tetr Asym 5 1727 (1994) (α -azido)
- Thermoanaerobium brockii* alcohol dehydrogenase Angew Int 23 151 (1984) (β -keto esters)
JACS 108 162, 3474 (4-, 5- and 6-chloro ketones) (1986)
JOC 52 256 (1987); 54 2646 (1989)
- Trichosporon capitatum* JOC 60 4324 (1995)
- horse liver alcohol dehydrogenase JACS 98 8476 (1976); 101 5405 (1979); 110 577 (1988)
Can J Chem 59 1574 (1981) (3-thiacycloalkanones)
TL 28 3059 (1987); 30 5313 (1989)
JOC 53 1611 (1988); 54 1795 (1989)
- lactate dehydrogenase JACS 104 4458 (1982); 110 2959 (1988) (both α -keto acids)
JOC 52 2608 (1987) (α -keto acid)
Can J Chem 67 1065 (1989) (α -keto acids)
CC 326 (1991) (α -keto acids)
TL 33 817 (2-oxo-3-alkenoic acids), 8159 (2,4-dioxoalkanoic acids to 2-hydroxy-4-oxoalkanoic acids) (1992)
- glycerol dehydrogenase JOC 51 25 (1986); 52 2608 (1987) (both α -hydroxy ketones)
- hydroxysteroid dehydrogenase JOC 56 67 (1991)
- various enzymes, yeasts, molds, fungi or bacteria Adv Carbohydr Chem 4 75 (1949) (review)
Appl Microbiol 11 389 (1963) (γ - and δ -keto acids)
BSCF 4217 (1972)
Angew Int 23 570 (1984); 24 539 (1985) (both reviews)
JACS 107 2993, 4028 (1985)
TL 27 2631 (β -keto esters), 2657 (β -keto esters), 4453 (α -diketones to diol) (1986); 28 1487 (aryl ketone), 3939 (β -keto esters), 5033 (4-O-benzyl-2-methyl-3-oxobutyrates esters) (1987); 33 7337 (1992) (α -chloro- β -keto esters); 35 3091 (1994) (β -keto ester)
JOC 52 256 (1987)



TL 30 3811 (1989)

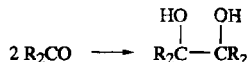


TL 35 5551 (1994)



TL 35 5621 (1994)

2.17. Pinacol Reaction



Reviews:

Chem Rev 88 733 (1988)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 3, Part 2.6, p 563

electrolysis

JACS 72 3797 (1950); 74 4260 (1952)
JOC 15 435 (1950); 31 3755 (1966); 33 294, 2145
(1968); 34 2807 (1969); 45 1710 (1980)
Acta Chem Scand 11 283 (1957)
JCS 863 (1958)
Chem Rev 62 19 (1962) (review)
JCS C 653 (1966); 2388 (1968)
Tetr 31 1925 (1975)
Helv 64 1570 (1981)
SL 757 (1990)

photolysis

Chem Rev 40 181 (1947) (review)

hν, Et₃N

TL 36 6915 (1995) (intramolecular)

hν, Et₃N, MeOH

TL 31 6793 (1990) (enones)

Li, NH₃

TL 28 1813 (1987); 29 2527 (1988)

Li, THF

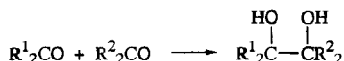
TL 28 1813 (1987); 29 2527 (1988)

Na

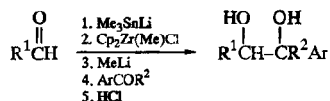
TL 3613 (1970); 36 5487 (1995)
JACS 108 1265 (1986)

Na(Hg)	JCS 2423 (1928) JACS 55 1179, 2827 (1933); 73 2586 (1951); 108 4561 (1986) TL 1879 (1964)
Mg-graphite	CC 1802 (1986)
Mg, I ₂	JOC 60 692 (1995) (intramolecular)
Mg, MgI ₂	JACS 49 236 (1927); 51 306 (1929) Chem Rev 57 417 (1957) (review)
Mg, Me ₃ SiCl, HMPA	TL 75 (1972)
Mg, HgCl ₂	Org Syn Coll Vol 1 459 (1941)
Me ₈ Sn ₃	TL 2847 (1978)
<i>n</i> -Bu ₃ SnH	JACS 117 7283 (1995) (intramolecular)
(Cl ₂ AlCl ₂) ₂ Ti·C ₆ Me ₆	JOC 41 260 (1976)
Cp ₂ TiCl ₂ , <i>sec</i> -BuMgCl	TL 28 5717 (1987)
CpTiCl ₃ , LiAlH ₄	JOC 41 260 (1976); 55 2959 (1990)
TiCl ₃	Chim Ind 67 187 (1985)
TiCl ₃ , NaOH	TL 23 3517 (1982)
TiCl ₃ , Li, ultrasound	JOC 56 1940 (1991)
TiCl ₃ , K	TL 23 5485 (1982)
TiCl ₃ , Zn-Cu	JACS 110 900 (1988); 111 8928 (1989) (intra- molecular); 112 6942 (1990) (intramolecular); 116 1591 (1994) (intramolecular); 117 634, 645 (1995) (both intramolecular) TL 30 1169, 1173 (1989); 35 4505 (1994) (intra- molecular) JOC 57 5692 (1992)
TiCl ₄ , <i>n</i> -BuLi	Chimia 40 12 (1986) (ArCHO)
TiCl ₄ , Mg	TL 29 5925 (1988) JOC 54 877 (1989) (enones)
TiCl ₄ , Mg(Hg)	JOC 41 260 (1976); 47 1657 (1982); 51 2969 (1986) TL 28 4965 (1987)
TiCl ₄ , Zn	CL 1041 (1973) TL 26 1983 (1985); 28 1799 (1987); 29 1161, 1399 (1988); 35 2709 (1994) (all intramolecular) JACS 110 6598 (1988); 112 5654 (1990) (intra- molecular); 115 4612 (1993) (intramolecular) JOC 58 5546 (1993) SL 293 (1993) (intramolecular)

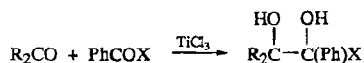
TiCl ₄ , Zn, py	JCS Perkin I 165 (1989) (intramolecular) JOC 56 282 (1990) TL 34 7005 (1993); 35 4959 (1994) (both intramolecular)
VCl ₃ , Zn	JOC 56 830 (1991) (intramolecular); 57 28, 5692 (1992)
Zn, HCl	JACS 107 686 (1985)
Zn, Me ₃ SiCl, lutidine	TL 24 2821 (1983) (intramolecular)
Zn, ZnCl ₂ , H ₂ O, THF	JOC 55 2981 (1990)
Ce, I ₂	TL 23 1353 (1982)
Sm, Me ₃ SiCl, NaI	JOC 59 7902 (1994)
Sm, Me ₃ SiBr	JOC 59 7902 (1994)
SmBr ₂	TL 34 2311 (1993)
SmI ₂	JOMC 250 227 (1983) TL 24 765 (1983); 32 1125, 5097 (1991); 35 2969, 6671 (1994) (both intramolecular); 36 2075, 6915 (1996) (both intramolecular) JOC 53 2132 (1988); 59 5532 (1994) (both intramolecular) JACS 111 8236 (1989) (intramolecular) SL 391 (1991) (intramolecular)



TiCl ₃	JOC 47 2852 (1982); 48 1690 (1983) Tetr 39 1239 (1983); 42 561 (1986) Chim Ind 67 187 (1985)
TiCl ₃ , Li	JOC 41 3929 (1976); 43 3255 (1978)
TiCl ₄ , Mg(Hg)	JOC 41 260 (1970)
[V ₂ Cl ₃ (THF) ₆] ₂ [Zn ₂ Cl ₆]	JACS 111 8014 (1989); 116 1316 (1994) JOC 55 4506, 5924 (1990); 57 782 (1992); 58 6114 (1993)
SmBr ₂	TL 34 2311 (1993)
Yb	JOC 53 6077 (1988)



JOC 58 7328 (1993)

X

COR IOC 54 3872 (1989)

CO₂Me TL 42 561 (1986)Me₃SiCl, Mg, HMPA TL 75 (1972)Me₃SiCl, Zn, ultrasound IOC 53 5871 (1988)Me₃SiBr, Yb TL 35 4111 (1994)CpFe(CO)₂K/Me₃SiCl/Δ (ArCHO) TL 34 2727 (1993)

3. Carboxylic Acids and Derivatives

Reviews:

Org Rxn 36 249 (1988) (aluminum hydrides)

J. Seyden Penne, "Reductions by the Alumino- and Borohydrides in Organic Synthesis," VCH-Lavoisier (1991), Chpt 2

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 8, Part 1.10, p 235

H₂, cat Ru-C, cat Re₂(CO)₁₀ TL 36 1059 (1995)H₂, cat Ru(acac)₃ or Ru₃(CO)₁₂, cat Re₂(CO)₁₀ TL 36 1059 (1995)H₂, cat Rh(acac)₃, cat Mo(CO)₆ or Re₂(CO)₁₀ TL 36 1059 (1995)H₂, cat Ru-Al₂O₃, cat Mo(CO)₆ TL 36 1059 (1995)H₂; cat Rh-Al₂O₃; cat Mo(CO)₆, W(CO)₆ or Re₂(CO)₁₀ TL 36 1059 (1995)H₂, cat Rh₆(CO)₁₆, cat Mo(CO)₆ or Re₂(CO)₁₀ TL 36 1059 (1995)H₂, cat Pd-C, cat Re₂(CO)₁₀ TL 36 1059 (1995)H₂, cat Pt-Al₂O₃, cat Re₂(CO)₁₀ TL 36 1059 (1995)BH₃ JACS 92 1637 (1970); 106 2160 (1984); 109 3098 (1987)




J Med Chem 13 203 (1970)

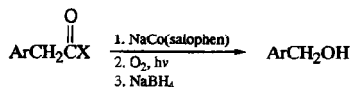
JOC 38 2786 (1973); 53 5552 (1988); 57 3007 (1992); 60 7503 (1995)

Org Syn 64 104 (1985)

Org Syn Coll Vol 7 221 (1990)

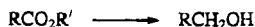
$\text{BH}_3 \cdot \text{SMe}_2$	JACS 101 6710 (1979) Org Prep Proc Int 13 225 (1981) (review) JOC 57 4352 (1992)
$\text{BH}_3 \cdot \text{SMe}_2$, $\text{BF}_3 \cdot \text{OEt}_2$	TL 3527 (1977) Org Syn 63 136 (1984); 68 77 (1989) Org Syn Coll Vol 7 530 (1990); 8 528 (1993) (all amino acids)
$\text{BH}_3 \cdot \text{SMe}_2$, B(OMe)_3	JOC 39 3052 (1974)
9-BBN	JOC 41 1778 (1976)
CB	JOC 42 512 (1977)
LiBH_4 , MeOH, diglyme	JOC 51 4000 (1986)
LiBH_4 , Me_3SiCl	Angew Int 28 218 (1989) Org Prep Proc Int 23 396 (1991) (amino acid)
NaBH_4	TL 35 7949 (1994)
NaBH_4 , $\text{BF}_3 \cdot \text{OEt}_2$	JOC 22 1135 (1957) JACS 110 2938 (1988)
NaBH_4 , AlCl_3	JACS 78 2582 (1956)
NaBH_4 , TiCl_4	Syn 695 (1980)
NaBH_4 , H_2SO_4	TL 33 5517 (1992) (amino acids)
NaBH_4 , MeSO_3H , DMSO	JOC 46 2579 (1981) (R = alkyl only)
NaBH_4 , I_2	JOC 56 5964 (1991); 58 3568 (1993) (amino acids); 58 4023 (1993) TL 36 2725 (1995) (α -hydroxy acid)
$\text{Zn}(\text{BH}_4)_2$	JOC 60 5314 (1995)
$\text{Zn}(\text{BH}_4)_2$, $(\text{CF}_3\text{CO})_2\text{O}$	JCS Perkin I 1561 (1992)
AlH_3	JACS 88 1464 (1966); 90 2927 (1968)
$\text{AlH}_3 \cdot \text{NMe}_2\text{Et}$	JOC 55 2968 (1990)
$\text{AlH}_3 \cdot \text{NEt}_3$	JOC 58 3974 (1993)
<i>i</i> -Bu ₂ AlH	Syn 617 (1975)
LiAlH_4	Org Rxn 6 469 (1951) (review) JACS 81 610 (1959); 108 4138 (1986); 109 7816 (1987) JOC 51 5019 (1986); 52 2337 (1987) Org Syn Coll Vol 7 530 (1990) (amino acid); 8 434 (1993) (α -chloro)
$\text{LiAlH}_4 \cdot \text{MeN} \begin{array}{c} \diagup \\ \diagdown \end{array}$	TL 35 1515 (1994)
LiAlH_4 , AlCl_3	JACS 81 610 (1959) JOC 59 2577 (1994)
NaAlH_4	JOC 58 4727 (1993)



$\text{NaH}_2\text{Al}(\text{OCH}_2\text{CH}_2\text{OCH}_3)_2$	Ind J Chem 12 290 (1974) JOC 47 5201 (1982)
 DCC/ NaBH_4	JCS Perkin I 2470 (1980)
$\text{RCOCl} \longrightarrow \text{RCH}_2\text{OH}$	
9-BBN	JOC 41 1778 (1976)
CB	JOC 42 512 (1977)
NaBH_4	JACS 71 122 (1949)
NaBH_4 , alumina	Syn 912 (1979)
NaBH_4 , AlCl_3	JACS 78 2582 (1956)
NaBH_4 , TiCl_4	Syn 695 (1980)
$\text{Zn}(\text{BH}_4)_2$, TMEDA	TL 27 4213 (1986)
LiH_3BN 	TL 33 4533 (1992)
$\text{LiH}_3\text{B}(n\text{-Bu})$	JOC 47 3311 (1982)
$\text{LiH}_3\text{BCRR}'\text{CN}$ ($\text{R}, \text{R}' = \text{H}, \text{H}; \text{H}, \text{Ph}; \text{Me}, \text{Me}$)	JOC 55 4464 (1990)
LiHBEt_3	JOC 45 1 (1980)
KHBET_3	Bull Korean Chem Soc 8 285 (1987)
$\text{KHB}(\text{sec-Bu})_3$	Bull Korean Chem Soc 10 382 (1989)
NaBH_3CN , ZnCl_2	JOC 50 1927 (1985)
$(n\text{-Bu}_4\text{N})\text{B}_3\text{H}_8$	TL 23 3337 (1982)
AlH_3	JACS 88 1464 (1966); 90 2927 (1968)
$\text{AlH}_3 \cdot \text{NMe}_2\text{Et}$	JOC 55 2968 (1990)
$\text{AlH}_3 \cdot \text{NEt}_3$	JOC 58 3974 (1993)
$i\text{-Bu}_2\text{AlH}$	JOC 50 2443 (1985)
LiAlH_4	JACS 69 1197 (1947); 81 610 (1959) Org Rxs 6 469 (1951) (review) Syn 901 (1981) JOC 58 6843 (1993) (RCOF)
LiAlH_4 , AlCl_3	JACS 81 610 (1959)
NaAlH_4	JOC 58 4727 (1993)
$\text{NaH}_2\text{AlEt}_2$	Bull Korean Chem Soc 13 199 (1992)
$\text{LiHAl}(i\text{-Bu})_2(n\text{-Bu})$	JOC 49 1717 (1984)
$\text{LiH}_2\text{InPh}_2$	TL 36 3169 (1995)
 NH/NaBH_4	JCS Perkin I 2470 (1980)





X = Cl, O₂CCH₂Ar

TL 29 707 (1988)



electrolysis	JOC 57 1061 (1992)
electrolysis, NH ₃	TL 28 1173 (1987)
Li or Na, NH ₃	JOC 44 2810 (1979)
Na, NH ₃ , EtOH	Ann 1532 (1982)
Na, EtOH	Helv 4 76 (1921) Org Syn Coll Vol 2 372 (1943)
Na, <i>t</i> -BuOH, HMPA	CC 567 (1978)
LiH, VCl ₃	JOC 45 1041 (1980)
BH ₃ ·SMe ₂	Syn 439 (1981) JOC 47 3153 (1982); 59 1166 (1994) TL 28 1147 (lactone), 3091 (1987); 30 6687 (1989) JACS 112 5276 (1990) (lactone) SL 41 (1992) (α-NHTs)
BH ₃ ·SMe ₂ , cat NaBH ₄	CL 1389 (1984) CC 992 (1987) TL 31 7323 (1990) JOC 58 7768 (1993); 60 7334 (1995) (all α-hydroxy esters)
9-BBN	JOC 41 1778 (1976)
CB	JOC 42 512 (1977)
LiBH ₄	Carbohydr Res 4 504 (1967) JOC 47 4702 (1982); 56 4706 (1991); 58 1696, 6596 (1993); 59 4875 (1994) TL 23 4991 (1982); 28 535, 4681 (lactone), 5458 (lactone) (1987); 33 2823 (1992) JACS 109 1186 (1987); 111 3382 (1989)
LiBH ₄ , MeOH	JOC 51 4000 (1986)
LiBH ₄ , cat MeOB  or B(OMe) ₃	JOC 47 1604 (1982); 49 3891 (1984)
LiBH ₄ , cat Li 	JOC 47 1604 (1982)
LiBH ₄ , cat LiHBEt ₃	JOC 47 1604 (1982) Syn 373 (1988)
LiBH ₄ , Me ₃ SiCl	Angew Int 28 218 (1989) (α-amino ester)

NaBH ₄ , H ₂ O, THF	TL 28 1147 (1987) (lactone) JOC 59 5930 (1994)
NaBH ₄ , MeOH	JOC 28 3261 (1963); 52 3777 (1987) TL 28 6069 (1987); 33 1647 (1992) (α -amido ester)
NaBH ₄ , EtOH	Chem Pharm Bull 13 995 (1965) (amino acid ester hydrochloride salts) TL 28 2265 (α -amino ester), 2709 (α -hydroxy ester) (1987) JACS 110 8134 (1988); 112 838 (1990) JOC 58 486 (1993) (α -hydroxy ester)
NaBH ₄ , <i>i</i> -PrOH	JACS 110 6467 (1988)
NaBH ₄ , <i>t</i> -BuOH	JACS 116 82 (1994)
NaBH ₄ , MeOH, <i>t</i> -BuOH	Syn Commun 12 463 (1982)
NaBH ₄ , polyethylene glycols	JOC 46 4584 (1981)
NaBH ₄ , LiCl, ROH	JOC 52 1252 (1987) TL 28 3671 (1987) JACS 111 6228 (1989)
NaBH ₄ , AlCl ₃	JACS 78 2582 (1956) JOC 60 2968 (1995)
NaBH ₄ , Me ₃ SiCl	Angew Int 28 218 (1989) (α -amino ester)
NaBH ₄ , MeSO ₃ H, DMSO (R = alkyl)	JOC 46 2579 (1981)
NaBH ₄ , cat CuSO ₄ (R = alkyl only)	SL 419 (1990)
Ca(BH ₄) ₂	JOC 47 4702 (1982) TL 28 5161 (1987) SL 311 (1992)
Zn(BH ₄) ₂ , ultrasound (R = alkyl)	TL 32 3243 (1991)
Zn(BH ₄) ₂ , cat PhNMe ₂ , ultrasound (R = Ar)	TL 32 3243 (1991)
NaBH ₃ OH	JOC 42 3963 (1977)
LiH ₃ BN 	TL 33 4533 (1992) JOC 59 6378 (1994)
LiH ₃ BN(<i>i</i> -Pr) ₂	JOC 59 6378 (1994)
NaH ₃ BNMe ₂	JOC 49 2438 (1984)
NaH ₃ BNH- <i>t</i> -Bu	JOC 49 2438 (1984)
LiH ₃ B(<i>n</i> -Bu)	JOC 47 3311 (1982)
LiHBEt ₃	JOC 45 1 (1980); 52 4352 (1987); 54 4280 (1989) CC 1786, 1797 (1987)
KHBEt ₃	Bull Korean Chem Soc 8 285 (1987); 10 205 (1989)

KHB(sec-Bu) ₃ (lactones > esters)	Bull Korean Chem Soc 10 120, 382 (1989)
AlH ₃	JACS 88 1464 (1966); 90 2927 (1968) BCSJ 55 3555 (1982) JOC 60 1806 (1995)
AlH ₃ ·NMe ₂ Et	JOC 55 2968 (1990)
AlH ₃ ·NEt ₃	JOC 58 3974 (1993)
<i>i</i> -Bu ₂ AlH	Ann 623 9 (1959) Syn 617 (1975) (review) JOC 49 1707 (1984); 50 2443 (1985); 52 1201 (1987); 54 1198 (1989); 57 5979 (1992) TL 27 5799 (1986) (lactone) JACS 110 879 (1988)
LiAlH(<i>i</i> -Bu) ₂ (<i>n</i> -Bu)	JOC 49 1717 (1984) JACS 109 5280 (1987) TL 32 5255 (1991)
LiAlH(<i>i</i> -Bu) ₂ (<i>n</i> -Bu)/NaBH ₄	TL 29 1057 (1988) (lactone)
NaH ₂ AlEt ₂	Bull Korean Chem Soc 13 199 (1992)
LiAlH ₄	JACS 69 1197 (1947); 107 2730 (1985); 108 468, 1019 (1986) Helv 31 1617 (1948); 32 1156 (1949) (both α -amino esters) Org Rxs 6 469 (1951) (review) Org Syn 63 140 (1984) JOC 50 2026 (1985); 52 5419, 5480 (1987) SL 41 (1992)
LiAlH ₄ ·MeN 	TL 35 1515 (1994)
LiAlH ₄ , BF ₃ ·OEt ₂	JOC 58 7490 (1993)
LiAlH ₄ , AlCl ₃	JACS 81 610 (1959); 92 3429 (1970); 105 3252 (1983); 109 6719 (1987) JOC 43 4915 (1978); 51 2863 (1986); 53 4877 (1988); 57 4598 (1992) SL 783 (1993)
NaAlH ₄	JOC 58 4727 (1993)
LiH ₃ AlO- <i>t</i> -Bu	JOC 59 5794 (1994)
LiAlH(OMe) ₃	JACS 87 5614 (1965); 113 2253 (1991) (α -hydroxy esters)
LiH ₃ InPh	TL 36 3169 (1995)
LiH ₂ InPh ₂	TL 36 3169 (1995)
HSi(OEt) ₃ , CsF/H ₃ O ⁺	Syn 558 (1981)
(EtO) ₂ SiMeH or Me ₃ SiO(MeSiHO) _n SiMe ₃ , KF or KO ₂ CH	Syn 981 (1982)

(EtO) ₃ SiH, cat Ti(O- <i>i</i> -Pr) ₄ /NaOH	JOC 57 3751 (1992)
cat Cp ₂ TiCl ₂ /cat <i>n</i> -BuLi/HSi(OEt) ₃ / NaOH or HCl	JACS 113 5093 (1991)
cat <i>n</i> -BuLi or EtMgBr, cat Cp ₂ TiCl ₂ / Me ₃ SiO(MeSiHO) _{<i>n</i>} SiMe ₃	IOC 59 4323 (1994)
Me ₃ SiO(MeSiHO) _{<i>n</i>} SiMe ₃ , Ti(O- <i>i</i> -Pr) ₄	SL 833 (1994) JOC 60 7884 (1995)
<i>i</i> -BuMgBr, cat Cp ₂ TiCl ₂	TL 21 2175 (1980)
SmI ₂ , base	TL 32 3511 (1991)



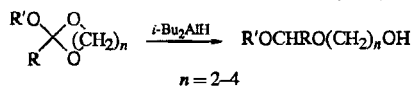
Li, NH ₃ , EtOH	JOC 37 2871 (1972); 57 5150 (1992)
NaBH ₄ , MeOH	JOC 28 3261 (1963)
LiAlH ₄	TL 1389 (1973); 32 2061 (1991)

Catalyst

amine	TL 34 8117 (1993)
PR ₃	TL 34 8117 (1993)
Ru ₃ (CO) ₁₂ , Me ₃ NO·2H ₂ O	TL 30 4137 (1989)
Ru ₃ (CO) ₁₂ , PR ₃	TL 30 6501 (1989) JOMC 387 315 (1990)
OsCl ₃ or Os(NH ₄) ₂ Br ₆ , amine	TL 33 3753 (1992)
Rh ₆ (CO) ₁₆	TL 28 2215 (1987)
IrCl(CO)(PPh ₃) ₂	Organomet 5 2497 (1986)



NaBH ₄	CC 330 (1978) Syn Commun 11 599 (1981) TL 23 3151 (1982)
NaBH ₄ , NiCl ₂ ·6H ₂ O	JOC 58 2407 (1993)
LiAlH ₄	JACS 108 4603 (1986) JOC 60 5910 (1995)



TL 29 1947 (1988)




BH_3 , cat LiCl

Bull Korean Chem Soc 7 296 (1986)

CB

JOC 42 512 (1977)

LiH_3BN 

TL 33 4533 (1992)

$\text{LiH}_3\text{B}(n\text{-Bu})$

JOC 47 3311 (1982)

AlH_3

JACS 88 1464 (1966)

$\text{AlH}_3 \cdot \text{NEt}_3$

JOC 58 3974 (1993)

LiAlH_4

JACS 69 1197 (1947)

TL 805, 2115 (1979)

$\text{LiAlH}_4 \cdot \text{MeN}$ 

TL 35 1515 (1994)

NaAlH_4

JOC 58 4727 (1993)

$\text{LiAl}(\text{OMe})_3$

JACS 87 5614 (1965)

$\text{LiAl}(\text{i-Bu})_2(n\text{-Bu})$

JOC 49 1717 (1984)

SmI_2 , KOH or LiNH_2

TL 32 3511 (1991)



Reagent

NaBH_4

J Med Chem 7 483 (1964)

Chem Pharm Bull 16 492 (1968); 27 816 (1979)

JACS 101 7109 (1979)

TL 27 6349 (1986); 30 6687 (1989); 32 923 (1991);

34 6513 (1993)

JOC 53 1900 (1988)

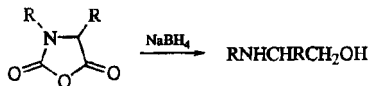
SL 595 (1992)

NaBH_4 , SmI_2

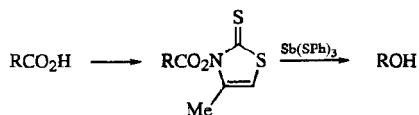
TL 28 5977 (1987)

LiBH_4

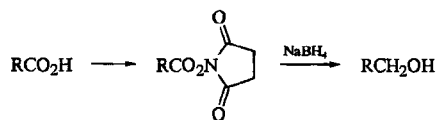
Z Naturforsch B 10 252 (1955)



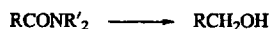
TL 35 569 (1994)



JOC 58 2468 (1993)



CL 981 (1979)



electrolysis

JOC 57 1061 (1992)

Na, *i*-PrOH

TL 35 1777 (1994)

 BH_3

Bull Korean Chem Soc 10 12 (1989)

9-BBN

JOC 41 1778 (1976)

 NaBH_4 , H_2O (imidazolides)

SL 839 (1995)



TL 33 4533 (1992); 34 1091 (1993)

JOC 59 6378 (1994)

 $\text{LiH}_3\text{BN}(i\text{-Pr})_2$

TL 34 1091 (1993)

 $\text{NaH}_3\text{BNMe}_2$

JOC 49 2438 (1984)

 $\text{NaH}_3\text{BNH-}i\text{-Bu}$

JOC 49 2438 (1984)

 LiHBEt_3

Syn 635 (1977)

JOC 45 1 (1980)

 KBHEt_3

Bull Korean Chem Soc 8 285 (1987)

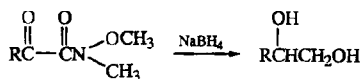
 LiAlH_4

JOC 18 1190 (1953)

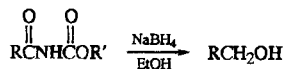
J Korean Chem Soc 35 296 (1991)

 SmI_2 , base

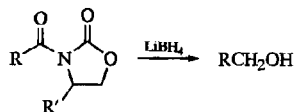
TL 32 3511 (1991)



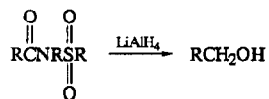
SL 497 (1992)



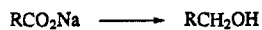
JACS 110 7249 (1988)



JACS 110 7910 (1988)



TL 30 5603 (1989)

 $\text{BH}_3 \cdot \text{THF}$

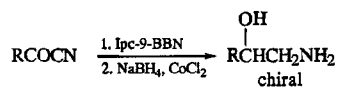
TL 23 2475 (1982)

CB

JOC 42 512 (1977)

 NaAlH_4

JOC 58 4727 (1993)



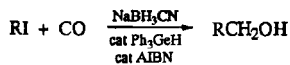
JOC 50 3237 (1985)



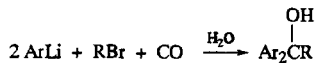
TL 34 4893 (1993)

9. ALKYLATION OF CARBONYL COMPOUNDS

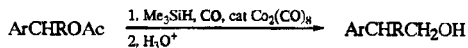
1. Addition to Carbon Monoxide



TL 34 591 (1993)



JOC 46 4625 (1981)



JOC 55 5923 (1990)

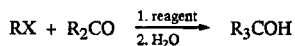
2. Addition to Aldehydes and Ketones

2.1. Organometallic Additions

Reviews:

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vols 1 and 2

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21b, G. Thieme, Stuttgart-New York (1995), pp 1151-1356



Reviews:

Syn 18 (1977) (reagent = Mg, Li, Ca, Zn)

C. Blomberg, "The Barbier Reaction and Related One-Step Processes," (Reactivity and Structure. Concepts in Organic Chemistry, Vol 31), Springer Verlag, Berlin-New York (1993)

Reagent	RX	
Li	1° alkyl	JOC 53 1212 (1988) (ultrasound)
	1°, 2°, 3° alkyl; allylic; benzylic; vinylic; aryl halides	JACS 102 7926 (1980) (ultrasound)
	1°, 2°, 3° alkyl; allylic; aryl halides	JCS Perkin I 1655 (1972)
	1° alkyl, allylic, aryl halides	CC 1160 (1970)
	2° alkyl chloride	CC 1319 (1986) (ultrasound)
	2° alkyl chloride, bromide, iodide	TL 28 2013 (1987) (ultrasound)
	2° alkyl bromide	JOC 59 2374 (1994) (ultrasound)
	3° alkyl bromide	JOC 59 922 (1994) (ultrasound)
	1° benzylic bromide	SL 319 (1995)
	3° benzylic chloride	CC 225 (1987) [(4- <i>t</i> -BuC ₆ H ₄) ₂ added]
	H ₂ C=CHCH ₂ Br	JACS 102 7926 (1980) (ultrasound)
	H ₂ C=CClCH ₂ Cl (both Cl)	TL 34 2011 (1993)
	bromobenzene	JCS Perkin II 378 (1976)
Li-Na	1°, 2°, 3° alkyl bromides	TL 29 3935 (1988); 30 4045 (1989)
Li, cat naphthalene	H ₂ C=C(CH ₂ Cl) ₂ (diol)	TL 33 2217 (1992)
Li, cat (4- <i>t</i> -BuC ₆ H ₄) ₂	CH ₃ OCH ₂ Cl	TL 34 3487 (1993)
RLi (R = Me, <i>n</i> -Bu)	R _f I	TL 31 5617 (1990)
Mg	1° alkyl, allylic, benzylic, propargylic, aryl halides	Syn 18 (1977) (review)
	Me ₂ N(CH ₂) ₃ Cl	Syn Commun II 241 (1981)
Mg, ultrasound	R _f I	TL 31 5617 (1990)
Mg, CuCl ₂ ·2H ₂ O	H ₂ C=CHCH ₂ X (X = Cl, Br)	TL 36 7119 (1995)
MgCl ₂ , (Me ₂ N) ₃ P	Cl ₃ CCO ₂ Me	BSCF II 207 (1983)
Ca	1° alkyl iodides	JOMC 66 219 (1974)
Et ₃ B, Ph ₃ SnH	α-bromo(iodo) ketone	TL 29 1041 (1988)
Al, Sn	RCH=CHCH ₂ X (X = Cl, Br)	Organomet 2 191 (1983) TL 26 6121 (1985)
	RCH=C(CH ₂ Br)CO ₂ Et	CL 541 (1986)
Al, SnCl ₂ , H ₂ O	RCH=CHCH ₂ Cl	JOC 50 5396 (1985) TL 27 2395 (1986)
Al, cat PbBr ₂	CX ₄ (X = Cl, Br), BrCCl ₃ , Cl ₃ CCONH ₂ , Cl ₃ CCN	JOC 54 444 (1989) TL 32 1031 (1991)
Al, BiCl ₃ , H ₂ O	RCH=CHCH ₂ Br	CC 708 (1987)


Al, HgCl ₂	HC≡CCH ₂ Br (alkynol)	JOC 58 7782 (1993)
Ga, LiCl, KI	BrCH ₂ CH=CHSiMe ₃ , BrCH ₂ C≡CSiMe ₃	TL 35 9433 (1994)
In	allylic chlorides, bromides, iodides and phosphates	JOC 53 1831 (1988); 58 5500, 7937 (1993); 59 3714 (1994) TL 32 7017 (1991); 36 2721, 6863 (1995) JACS 114 8841 (1992)
	H ₂ C=C(CH ₂ Br) ₂ (diol) H ₂ C=C(CH ₂ Br)CO ₂ H	TL 36 517 (1995) JOC 60 4228 (1995)
GeI ₂ , ZnI ₂	allylic bromides, propargyl bromide	TL 35 4805 (1994)
Sn	XCR ₂ CO ₂ R (X = Cl, Br) RCOCR ₂ Br allylic chlorides, bromides and iodides H ₂ C=CHCF ₂ Br (rearrange- ment)	CL 161, 929 (1982) CL 467 (1982); 1727 (1983) CL 1527 (1981); 541 (1986) TL 36 2721 (1995) JOC 56 1037 (1991)
Sn, ultrasound	H ₂ C=CHCH ₂ Br	TL 26 1449 (1985)
Sn, electrolysis	H ₂ C=CHCH ₂ Br	TL 25 6017 (1984)
Sn, H ₂ O	H ₂ C=CXCH ₂ Br (X = H, Br, OAc)	Organomet 2 191 (1983) JOC 49 172 (1984); 58 5500 (1993) JACS 113 6674 (1991) CL 541 (1986)
Sn, Me ₃ SiCl, NaI, H ₂ O	RCH=C(CH ₂ Br)CO ₂ Et	JOC 57 6988 (1992)
SnF ₂	H ₂ C=CHCH ₂ I CBr ₄	CL 1507 (1980); 1109 (1981); 929 (1982) CL 1505 (1981)
SnCl ₂	H ₂ C=CHCH ₂ I	Tetr 37 3873 (1981)
SnCl ₂ , chiral EtO ₂ CCH(ONa)- CH(ONa)CO ₂ Et	H ₂ C=CHCH ₂ Br	CC 685 (1986) JOC 52 5447 (1987)
SnCl ₂ , cat PdCl ₂ (PhCN) ₂	allylic alcohols allylic carbonates allylic acetates	JACS 110 4473 (1988); 114 2577 (1992) TL 30 3437 (1989) TL 29 3563 (1988) CC 44 (1988)
SnI ₂ , Me ₃ SiCl, NaI, H ₂ O	allylic iodide	JOC 57 6988 (1992)
Sb	H ₂ C=CHCH ₂ I	TL 28 3707 (1987)
Sb, LiI	H ₂ C=CHCH ₂ X [X = Br, OPO(OPh) ₂]	TL 28 3707 (1987)
R ₃ Sb (R = Et, <i>n</i> -Bu), (cat I ₂)	allylic chlorides, bromides, iodides	TL 29 1395 (1988)
<i>n</i> -Bu ₃ Sb	Cl ₃ CCN	TL 29 5275 (1988)

Reagent	RX	
Bi	$\text{H}_2\text{C}=\text{CHCH}_2\text{X}$ (X = Br, I)	TL 26 4211 (1985)
BiCl_3 , Zn or Fe	$\text{R}_2\text{C}=\text{CHCH}_2\text{X}$ (X = Cl, Br, I)	TL 27 4771 (1986)
$\text{Ti}(\text{O}-i\text{-Pr})_4$, $i\text{-PrMgBr}$	$\text{H}_2\text{C}=\text{CHCH}_2\text{X}$ [X = Cl, Br, I, OTs, OPh, OAc, OCO_2Et , $\text{OPO}(\text{OEt})_2$]	JACS 117 3881 (1995)
Cp_2TiCl_2 , $n\text{-BuLi}$	allylic phenyl sulfides	TL 36 1495 (1995)
CrCl_2	RSCH_2Cl	JOC 51 5045 (1986)
	allylic halides	TL 33 4761 (1992)
		JOC 58 2931 (1993)
		SL 498 (1995)
	allylic phosphates	JOC 57 6384 (1992)
	allylic mesylates	JOC 57 6384 (1992)
	$\text{RCH}=\text{CHCHCl}_2$ (R = $\text{CHRCH}=\text{CHCl}$)	TL 30 4389 (1989)
	ArI , $\text{RCH}=\text{CRX}$ (X = Br, I)	TL 24 5281 (1983)
	$\text{RC}\equiv\text{CX}$ (X = Br, I)	TL 26 5585 (1985); 34 1467 (1993) (intramolecular)
CrCl_2 , LiH	$\text{RC}\equiv\text{CCH}_2\text{Cl}(\text{Br})$ (allene)	JOC 57 4070 (1992)
	$(\text{RCO})_2\text{NCH}_2\text{X}$ (X = Cl, Br, I)	JOC 58 588 (1993)
CrCl_2 , cat vitamin B_{12} or cobalt phthalocyanine	1° alkyl iodide or tosylate	JOC 54 4732 (1989)
CrCl_2 , cat $\text{Ni}(\text{acac})_2$	$\text{RCH}=\text{CHI}$	JACS 110 5198 (1988) (intramolecular)
CrCl_2 , cat NiCl_2	review	Pure Appl Chem 64 343 (1992)
	$\text{RCH}=\text{CROTf}$	JACS 108 6048 (1986); 117 10239 (1995)
		TL 34 6003 (1993) (inter- and intramolecular)
	$\text{RCH}=\text{CHI}(\text{Br})$	JACS 108 5644 (1986); 111 2735 (intramolecular), 7525 (1989); 114 3162, 10653 (intramolecular) (1992); 115 2970, 11393 (intramolecular) (1993); 117 6224, 10391 (1995)
		JOC 52 4823 (1987); 53 3383 (1988)
		TL 29 4909 (1988) (intramo- lecular); 33 1549 (1992); 34 3993, 5999 (intramolecular), 6003 (inter- and intramolec- ular) (1993); 35 2087, 9207, 9581 (1994); 36 3763, 5357, 8103 (intramolecular) (1995)
		SL 599 (1992); 189 (1993)

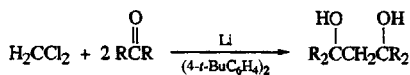
	$RC\equiv C(I)(Br)$	TL 28 3463 (1987); 32 3171 (1991) (intramolecular haloalkynal); 33 7511 (1992) (intramolecular haloalkynal); 36 3197, 5167 (1995) (both intramolecular haloalkynal) JACS 114 9279 (1992) (intramolecular haloalkynal); 115 12621 (1993); 116 5511 (1994) JOC 58 4202 (1993) (intramolecular haloalkynal); 59 88 (1994) SL 54, 485 (intramolecular haloalkynal) (1994) JOC 60 5386 (1995)
$CrCl_2$, cat $NiCl_2$, chiral ligand (enantioselective)	$H_2C=CHCH_2Br$, $RCH=CHI$	JACS 108 5644 (1986)
$CrCl_2$, cat $Pd(OAc)_2$	$RCH=CHI$	Syn 248 (1992)
$CrCl_2$ or $CrCl_3-LiAlH_4$	review allylic bromides, iodides, phosphates and tosylates	JACS 99 3179 (1977); 107 5219 (1985); 112 4078 (intramolecular haloalkenal), 5290, 5369 (intramolecular haloalkenal) (1990); 113 4218, 8791 (1991); 114 3910, 3926 (intramolecular haloalkenal) (1992); 117 1908 (1995) TL 1685 (1978); 22 1037 (1981); 23 2343 (1982); 27 4957, 5091 (1986); 28 5615 (1987); 29 2923, 6107 (1988); 31 6605 (1990); 35 3183 (1994) Tetr 37 3873 (1981) BCSJ 55 561 (1982) CL 85 (1986) (intramolecular) JOC 52 316 (1987); 53 4098 (1988); 54 3009, 3515, 6129 (1989); 56 461 (1991); 58 165 (1993) (intramolecular haloalkenal); 59 3347 (1994); 60 2762 (1995) JCS Perkin I 165 (1989) SL 444 (1992); 293 (1993); 337 (1994)
$Ph_2Cr-TMEDA$	allylic bromides and iodides, propargyl bromide	CC 1654 (1993)
Mn	$RCH=CHCH_2X$, (X = Cl, Br)	Organomet 1 1249 (1982) TL 30 7373 (1989) TL 30 7373 (1989)
	$BrCR_2CO_2R$	CL 1237 (1983)
Mn, I_2	$H_2C=CHCH_2Br$	

Reagent	RX	
Co(PMe ₃) ₄	(Cl)BrCHRX (X = CO ₂ R, CONR ₂ , CN)	JOC 59 1 (1994)
cat NiBr ₂ (bipy), electrolysis	ClCH ₂ CO ₂ Me; allylic chlorides and acetates	TL 28 55 (1987) JOC 54 2198 (1989)
cat Ni(bipy) ₃ (BF ₄) ₂ , electrolysis	RCHClCO ₂ R, RCHClCN	JOC 56 2018 (1991)
Zn	reviews	"Methods of Elemento-Organic Chemistry," North-Holland, Amsterdam (1967), Vol 3 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 1.8, p 277
	CF ₃ X (X = Br, I)	CC 642 (1987) JCS Perkin I 1951 (1990) TL 33 4279 (1992)
	R ₂ I	JOC 53 2349 (1988)
	ClCH ₂ COR	TL 29 2291 (1988) (intramolecular)
	RCHBrCOR	JACS 89 5727 (1967)
	RCHXCO ₂ R	Org Rxs I 1 (1942); 22 423 (1975) (both reviews) Org Syn Coll Vol 4 444 (1963) JOC 34 3689 (1969); 39 269 (1974); 46 4323 (1981); 48 4108 (1983); 52 5745 (intramolecular) (1987); 53 893, 1010 (1988); 54 1992 (1989); 56 2018, 4333 (1991) Organomet Chem Rev A 8 183 (1972) (review) Syn 452 (1975); 571 (1989) (review) BSCF II 145 (1980) Acta Chem Scand B 35 273 (1981) (chiral RO ₂ CCH ₂ Br) JACS 108 1617 (1986); 111 2342 (1989) (ultrasound); 114 8464 (1992) TL 28 6145 (1987); 33 4605 (1992)
	MeCFBrCO ₂ Et	JOC 58 3483 (1993)
	ClCF ₂ COX (X = R, OR, NHR)	TL 29 2943 (1988)
	BrCF ₂ CO ₂ Et	TL 25 2301 (1984); 29 3687 (1988); 30 4259 (1989); 34 7195 (1993) JOC 53 2406 (1988); 57 7309 (1992); 58 5724 (1993)
	ICF ₂ CO ₂ Me	TL 29 1803 (1988)

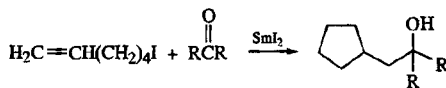
	RCHBrCONR ₂	JOC 52 5745 (1987) (intramolecular)
	BrCH ₂ CN	JOC 56 2018 (1991)
	BrCH ₂ CR=CHCO ₂ R'	TL 27 5193 (1986)
	(R = H, Me)	JOC 54 1992, 3533 (1989)
	allylic halides	JOC 41 551 (1976); 47 3148 (1982); 48 4108 (1983); 50 2011 (1985); 56 4333 (1991); 59 1444 (1994)
		TL 28 3151, 4551 (1987); 33 97 (1992); 36 4257, 4885 (1995)
		SL 627 (1990)
		JACS 116 2211 (1994)
		JOC 56 1037 (1991)
	H ₂ C=CHCF ₂ Br (rearrange- ment)	
	RCH=C(CH ₂ Br)SO ₂ Ph	TL 27 5091 (1986)
	H ₂ C=CHCH=CHCH ₂ Br	TL 27 5211 (1986)
	[R = (H ₂ C=CH) ₂ CH]	
	(BrCH ₂) ₂ C=CHCH ₂ Br	TL 34 7607 (1993)
	[R = CH ₂ C(=CH ₂)- CH=CH ₂]	
	propargylic halides	Syn Commun 10 637 (1980)
		JACS 115 9421 (1993)
		JOC 60 3257 (1995)
Zn, ultrasound	CF ₃ I	Chem Pharm Bull 39 2459 (1991)
	R _f I	CL 1679 (1981)
	BrCH ₂ CO ₂ Et	JOC 47 5030 (1982); 54 2183 (1989)
	BrCH ₂ CH=CHCO ₂ Me	JOC 55 3537 (1990)
	H ₂ C=CHCH ₂ Br	TL 26 1449 (1985)
Zn, ultrasound, H ₂ O	R ₂ C=CHCH ₂ X (X = Cl, Br)	JOC 50 910 (1985)
Zn, ultrasound, (Cp ₂ TiCl ₂)	R _f Br(I)	JACS 107 5186 (1985)
Zn, NH ₄ Cl, C ₁₈ -silica	allylic chlorides and bromides	JOC 54 3087 (1989)
Zn, B(OMe) ₃	BrCH ₂ CO ₂ R	JOC 35 3966 (1970)
		JACS 107 3891 (1985)
		Tetr 50 3235 (1994)
Zn, Me ₃ SiCl	XCH ₂ CN (X = Cl, Br)	TL 31 2205 (1990)
	BrCH ₂ CO ₂ R	JOC 52 4796 (1987)
		TL 31 6425 (1990); 32 3417 (1991)
	BrCH ₂ CON(Me)OMe	TL 32 2525 (1991)
Zn, cat TiCl ₄	HC≡CCH ₂ Br	JOC 55 5324 (1990)
Zn, cat Cp ₂ TiCl ₂	allylic bromides	TL 33 8117 (1992)
Zn, cat MCl ₂ (PPh ₃) ₂ (M = Ni, Pd)	R _f I	CL 517 (1984)
Zn, cat Pd(PPh ₃) ₄	allylic acetates	JOC 52 3702 (1987) (RCHO only)

Reagent	RX	
Zn, cat viologen	R_3I	JOC 53 2349 (1988)
Zn-Cu	$BrCH_2CO_2Et$	Syn 698 (1977)
	$BrCHRCO_2Et$	TL 34 5641 (1993)
	$BrCH_2CH=CHCO_2R$	JOC 52 4397 (1987)
	allylic bromide	JOC 58 2931 (1993)
Zn-CuCl	$ClCF_2COR$	TL 28 6481 (1987)
	$H_2C=CBBrCF_3$	CC 289 (1994)
Zn, CuCl, ultrasound	$H_2C=CBBrCF_3$	SL 199 (1995)
Zn-CuCl or Zn-AgOAc	$ClCF_2C(=CH_2)CH_2SiMe_3$	TL 32 1069 (1991)
Zn-Cu(OAc) ₂	$ClCF_2CH=CHCO_2Et$ (rearrangement)	SL 977 (1992)
Zn-Ag, ultrasound		CC 1552 (1987)
Zn-Ag graphite	$RCHXCO_2R$ (X = Cl, Br)	CC 775 (1986)
Zn, AgOAc, Et ₂ AlCl	$ClCF_2COR$	TL 28 6481 (1987)
	$BrCH_2CO_2R$	BCSJ 53 3301 (1980)
	$BrCF_2CO_2Et$	JOC 58 6360 (1993)
Zn, ZnCl ₂	$RCHBrCO_2R$	JOC 60 1120 (1995) (intramolecular)
Zn-Hg	$HC\equiv CCH_2Br$	SL 493 (1995)
Zn, cat HgCl ₂	$RC\equiv CCF_2Br$	TL 28 659 (1987)
Zn / MeLi	aryl iodides	JOC 59 4717 (1994)
Et ₂ Zn, cat Pd(PPh ₃) ₄	$H_2C=CHCH_2X$ (X = O ₂ CPh, OPh)	TL 34 7619 (1993)
Me ₃ ZnLi	aryl iodides	JOC 59 4717 (1994)
Cd	$H_2C=CHCF_2Br$	JOC 56 1037 (1991)
Cd, n-Bu ₄ NBr	allylic bromides and iodides	TL 33 4795 (1992)
Cc(Hg)	benzylic and propargylic (alkynol and alkadienol) iodides	JOC 49 3904 (1984)
	allylic bromides and iodides	TL 22 4987 (1981)
		JOC 49 3904 (1984)
Sm	CH_2I_2	TL 27 3243 (1986)
Sm, Me ₃ SiCl, NaI	$BrCH_2CO_2Et$, $H_2C=CHCH_2I$	JOC 59 7902 (1994)
SmI ₂	mechanism	SL 943 (1992) (review)
	1° alkyl iodides, bromides, tosylates; allylic; propargyl (alkynol and alkadienol); benzylic halides;	JACS 102 2693 (1980); 114 6050 (1992); 116 9912 (1994)
	$RCHBrCO_2R$	

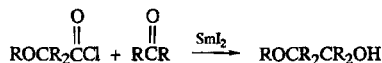
1° alkyl iodide	TL 34 1717 (1993)
benzylic bromide	JACS 112 8090 (1990 haloalkanal); 115 5466 (1993) haloalkanone (both intramolecular)
allylic bromide	TL 33 4345 (1992)
benzylic bromides, allylic halides	JOMC 250 227 (1983)
allylic bromides and iodides, benzylic bromides	TL 23 3497 (1982)
CH ₂ X ₂ (X = Br, I)	TL 27 3891 (1986)
PhCH ₂ OCH ₂ Cl	JOC 58 4262 (1993)
	TL 25 3225 (1984); 29 4847 (1988)
RC≡Cl	JACS 109 4424 (1987)
ClCH ₂ COR	TL 36 3707 (1995)
BrCHRCO ₂ R	TL 29 2291 (1988) (intramolecular)
RCH(O ₂ CPh)CO ₂ R	intramolecular reactions are listed later in this section
RCOCl	TL 33 313, 6069 (1992)
	JOC 58 4061 (1993)
	TL 25 2869 (1984); 29 4847 (1988)
SmI ₂ , cat Pd(PPh ₃) ₄	allylic acetates
	TL 27 1195 (1986)
	RC≡CCH ₂ OPO(OEt) ₂ (alkynol)
	TL 36 907 (1995)
cat SmCl ₃ , electrolysis	allylic chlorides
	TL 34 1475 (1993)
Cp* ₂ Sm(THF) _n (n = 0, 2)	allylic benzyl ethers
	TL 36 1505 (1995)



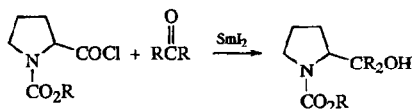
TL 35 253 (1994)



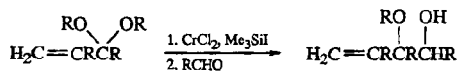
JOC 55 6171 (1990)



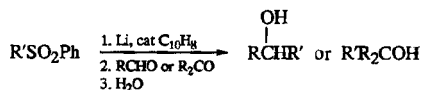
TL 29 4847 (1988)



TL 33 2973 (1992)

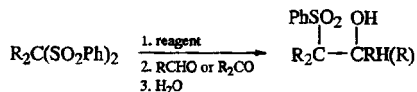


TL 29 5263 (1988)



R' = 1°, 2° alkyl; allyl; benzyl

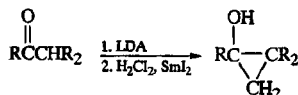
TL 35 2965 (1994)

ReagentLiC₁₀H₈

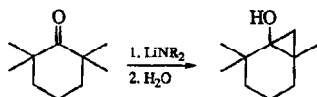
TL 35 5437 (1994)

SmI₂

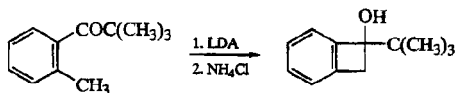
TL 35 5441 (1994)



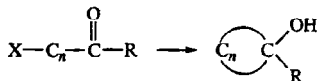
TL 28 1307 (1987)



JACS 110 957 (1988)



TL 36 733 (1995)



n

X

Reagent(s)

2

Br

SmI₂

TL 32 7691 (1991)

3

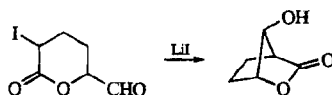
Br

Mg

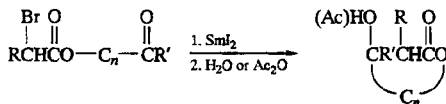
CC 890 (1968)

BSCF 359 (1968)

3, 4	Br	Mg(Hg)	Compt Rend C 265 1472 (1967)
4	Br	Mg or Ca, NH ₃ SmI ₂	Can J Chem 58 2524 (1980) TL 29 171 (1988) JOC 53 2327 (1988)
	I	Mg	Ber 35 2684 (1902) JOC 47 5368 (1982)
		Mg, HgCl ₂	TL 28 3963 (1987)
		<i>n</i> -BuLi	TL 28 3963 (1987)
		<i>n</i> -Bu ₂ CuLi	TL 28 5071 (1987)
		SmI ₂	TL 28 3963 (1987) Syn Commun 17 901 (1987)
4, 5	I	SmI ₂ , [cat Fe(PhCOCHCOPh) ₃]	TL 25 3281 (1984) JOC 51 1778 (1986); 56 4112 (1991) JACS 109 453 (1987)
5	Br	Mg	CC 1287 (1968) Angew Int 20 576 (1981)
		SmI ₂	JACS 109 6559 (1987)
	I	<i>n</i> - or <i>t</i> -BuLi	TL 26 4987 (1985); 34 2095 (1993) JOC 51 1778 (1986)
		SmI ₂	JOC 50 2759 (1985)
		SmI ₂ , Zn	TL 31 5599 (1990)
5, 6	I	nickel tetraphenylporphine, Li naphthalene	JACS 92 395 (1970)

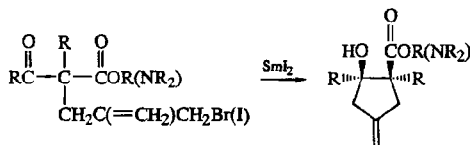


TL 32 6227 (1991)

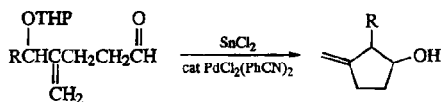


TL 27 3889 (1986); 29 6947 (1988); 32 6371 (1991); 36 6515, 6519 (1995)
JACS 109 6556 (1987); 113 8036 (1991)

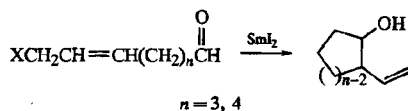
For analogous reactions using Zn, see pages 1130–1132.



JACS 109 453 (1987)



TL 33 6477 (1992)

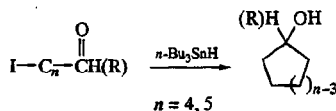
X

SPh

JOC 59 5111, 5532 (1994)

SO₂Ph

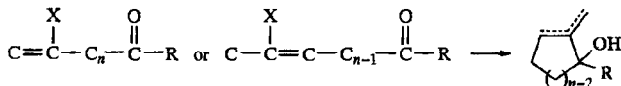
JOC 59 5111 (1994)



JACS 108 2116, 8102 (1986); 109 3484 (1987); 113 5791 (1991)

TL 29 1645 (1988); 34 6247 (1993)

JOC 57 4954 (1992)

XRing SizeReagent(s)

Br

5

n-Bu₃SnH

TL 34 7283 (1993)

6

Li

JACS 104 6879 (1982)

t-BuLi

TL 36 4939 (1995)

I

5

n-Bu₃SnSiMe₃, CsF

JOC 58 2972 (1993); 60 115 (1995)

n-Bu₃SnSiMe₃, *n*-Bu₄NCl

TL 32 6139 (1991)

R₂CuLi

JACS 92 395 (1970)

5, 6

n-BuLi

TL 23 4987 (1985); 29 4053 (1988); 35 8573 (1994)

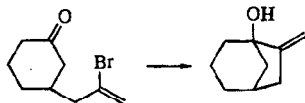
JOC 58 11 (1993)

6

Mg

JOC 51 3405 (1986)

See also page 1128 for intramolecular examples using chromium reagents.

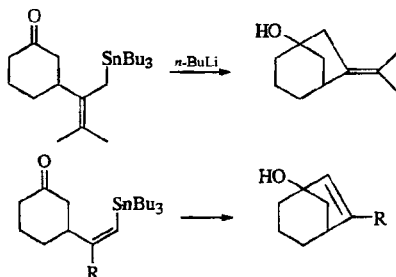
*n*-Bu₂CuLi

JACS 92 396 (1970)

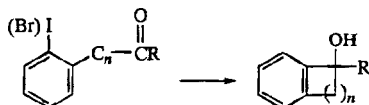
TL 23 3291 (1982)

SmI₂

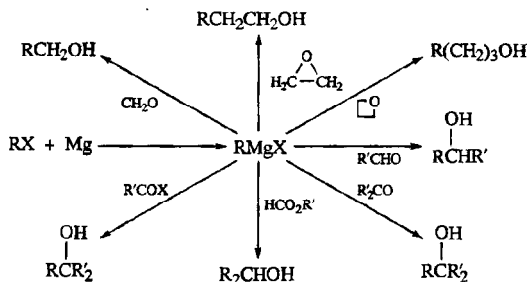
TL 33 6931 (1992)



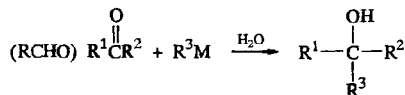
TL 33 5841 (1992)


Reagent(s)

Reagent(s)	<i>n</i>	
Li	2	TL 35 4771 (1994)
<i>n</i> -BuLi	1,3	TL 31 5347 (1990); 32 2171 (1991) JOC 60 588 (1995)
<i>n</i> -Bu ₃ SnSiMe ₃ , [(Et ₂ N) ₃ S]Me ₃ SiF ₂	2	JOC 58 2972 (1993)
<i>n</i> -Bu ₃ SnSiMe ₃ , (PhCH ₂ NEt ₃)Cl	2	TL 32 6139 (1991)



Review: M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, Englewood Cliffs, New Jersey (1954)


Reviews:

M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, Englewood Cliffs, New Jersey (1954)
 JOC 39 3258 (1974) (organometallic "ate" complexes of Li, B, Al, Mg, Zn)
 Chem Rev 75 521 (1975) (stereochemistry)

- "Organometallic Chemistry Reviews," Vol 3 (1977)
 J. C. Stowell, "Carbanions in Organic Synthesis," J. Wiley, New York (1979)
 R. L. Augustine, "Carbon-Carbon Bond Formation," Vol 1, Marcel Dekker, New York (1979)
 E. Negishi, "Organometallics in Organic Synthesis," J. Wiley, New York (1980)
 Pure Appl Chem 52 545 (1980) (mechanism of Grignard addition to ketones)
 JACS 103 4540 (1981); 111 8447 (1989) (both stereochemistry of cyclohexanone additions)
 Syn 605 (1982) (stereoselectivity of addition to chiral aminocarbonyl compounds)
 CC 452 (1982) (stereoselectivity of various R^3M on α -chiral ketone)
 E. L. Eliel in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York, Vol II, Part A (1983), p 125
 Angew Int 23 556 (1984) (chelation and non-chelation control in addition reactions of chiral α - and β -alkoxy carbonyl compounds); 30 49 (1991) (enantioselectivity)
 TL 32 1937 (1991) (MeM stereoselectivity); 35 4645 (1994) (various RM)
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vols 1 and 2
 Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21b, G. Thieme, Stuttgart-New York (1995), Section 1.3 (enantioselective)

 R^3M

RLi

- JACS 81 2748 (1959) (stereochemistry); 97 5280 (1975) (stereochemistry); 101 1455 (1979) (asymmetric); 103 4540 (stereochemistry); 4585 (chiral catalysis) (1981); 107 6411 (1985) (stereochemistry); 111 7265 (1989) (asymmetric); 112 7299 (1990)
 CC 1160 (1970); 1600 (1986) (α -alkoxy or -siloxy ketone diastereoselectivity)
 JCS Perkin I 1655 (1972)
 JOC 38 904 (1973); 40 1469 (1975) (stereochemistry); 43 1064, 2173 (stereochemistry) (1978); 46 2798 (1981) (chiral catalysis); 53 2465, 2477, 2482, 4555 (1988); 54 4158 (1989); 55 5404 (1990)
 JCS Perkin II 378 (1976)
 TL 2659 (1976) (stereochemistry); 1709 (1977) (stereochemistry); 28 2629 (1987); 33 5597 (1992); 35 1969 (1994)
 CL 219 (1978) (asymmetric)
 Helv 62 1701, 1710, 2695 (1979)
 Tetr 38 2725 (1982) (stereoselectivity using chiral ligand)

RLi, LiClO₄

- JOC 44 4371 (1979)

RLi, *n*-Bu₄NBr

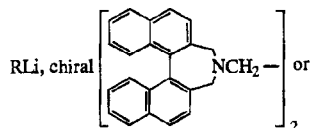
- CC 923 (1987) (Cram selective)

RLi, crown ether

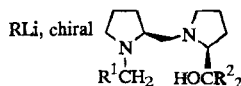
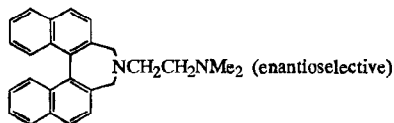
- JACS 107 6411 (1985) (stereochemistry)

RLi, chiral Me₂NCH₂CH(OMe)CH(OMe)-CH₂NMe₂ and related chiral solvents (enantioselective)

- Helv 60 301 (1977); 62 1701, 2695 (1979)
 Org Syn Coll Vol 7 451 (1990)



JACS 103 4585 (1981)



JACS 101 1455 (1979)

Tetr 37 4111 (1981)

MAD/RLi

JACS 107 4573 (1985); 110 3588 (1988)

(aldehydes and cyclic ketones only, axial addition)

TL 28 1439 (1987); 29 3101 (1988)

($\text{RCHO} \gg \text{R}_2\text{CO}$)

SL 683 (1993); 441 (1994) (less hindered ketone > more hindered ketone)

JOC 59 3142 (1994)

$(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_2\text{AlMe}$ /RLi

JACS 115 1182 (1993) (more hindered of two aldehydes)

$(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_3\text{Al}$ /RLi

SL 441 (1994) (more hindered ketone > less hindered ketone)

$\text{Me}_2\text{AlNMePh}$ /RLi

TL 29 3101 (1988) ($\text{R}_2\text{CO} \gg \text{RCHO}$)

MeLi

JACS 107 4573 (1985) (stereochemistry)

JOC 50 422 (1985)

TL 31 4565, 5479 (1990); 33 1759 (1992)

n-BuLi, chiral lithium amides (enantioselective)

TL 25 5187 (1984)

ArLi

JOC 57 5166 (1992)

TL 34 1553 (1993)

o-Me₃SiC₆H₄Li

TL 35 579 (1994)

LiCH₂OCH₂OMe

JOC 53 4131 (1988); 55 5625 (1990)

LiCR₂OR'

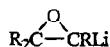
TL 21 1285 (1980); 24 3165 (1983); 28 4131 (1987)

JACS 100 1481 (1978); 102 6900 (1980); 106 3376

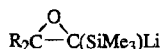
(1984); 107 3285 (1985); 110 842, 854 (1988);

116 8795 (1994); 117 10889 (1995) (chiral)

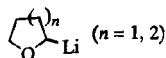
JOC 58 6009 (1993)



TL 32 615 (1991); 36 8235 (1995)



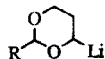
JOC 54 4042 (1989)

R³M

JACS 102 6900 (1980); 106 1130 (1984)

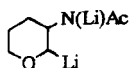
TL 30 3011 (1989); 35 715 (1994)

JOC 59 3142 (1994)



JOC 57 4336 (1992)

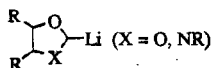
TL 35 6799 (1994)



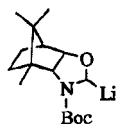
TL 35 6067 (1994)



JACS 111 1381 (1989)



TL 35 2063 (1994)

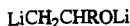


TL 36 2863 (1995)



Angew Int 15 738 (1978)

Ber 113 1290, 2055 (1980)



JOC 55 1528 (1990)

TL 34 5553 (1993)



Ber 113 1290 (1978)

JOC 54 5657 (1989)



JOC 56 5760 (1991)



JOC 56 5760 (1991)

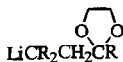


JACS 113 1866 (1991)



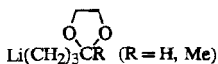
CC 425 (1987)

SL 209 (1995)



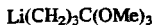
JOC 57 6 (1991)

SL 209 (1995)



TL 31 3763, 3767 (1990)

JOC 56 3825 (1991); 57 750 (1992)



SL 601 (1990)



TL 32 1975 (1991)



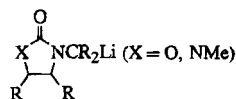
TL 34 1649 (1993)



JOC 54 5651 (1989)



JOC 58 255 (1993)



$\text{LiCH}_2\text{CHRN}(\text{Li})\text{COPh}$

$\text{LiCR}_2\text{CO}_2\text{Li}$

$\text{LiCR}_2\text{CO}_2\text{R}$

$\text{LiCN}_2\text{CO}_2\text{Et}$

$\text{LiCR}_2\text{CONR}_2$

LiCR_2CN

homoallylic Li

$\text{LiCH}=\text{CH}_2$

$\text{LiCH}=\text{CF}_2$

$\text{LiC}(\text{CF}_3)=\text{CF}_2$

$\text{LiCR}=\text{CHR}$

JOC 54 5651 (1989)

JACS 113 8546 (1991); 115 2622 (1993)

TL 29 2859 (1988); 35 4831 (1994)

See page 1717, Section 1.

See page 1724, Section 2.

JOC 55 4144 (1990)

See page 1778, Section 4.

See page 1801, Section 6.

JACS 115 3855 (1993)

TL 33 1697 (1992)

TL 34 7565 (1993)

TL 36 3973 (1995)

TL 4839 (1976); 22 3745 (1981); 31 1857 (1990)

Ber 111 2785 (1978)

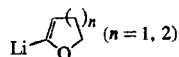
JACS 110 890 (1988); 112 1897, 5562 (1990); 113 5365 (1991)

JOC 53 2214 (1988); 55 4784 (1990); 56 3831

(1991); 57 2007, 2523 (1992); 58 4989 (1993); 59 1586, 2033 (1994)

SL 645 (1994)

$\text{LiC}(\text{OR})=\text{CH}_2$



See page 351, Section 1.

TL 4187 (1977); 34 5693, 8019 (1993)

Tetr 37 3997 (1981)

Heterocycles 30 765 (1990)

JACS 113 5073 (1991); 114 9419 (1992)

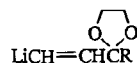
JOC 57 3947, 3956 (1992)

$\text{LiCH}=\text{CHCH}_2\text{OLi}$

$\text{H}_2\text{C}=\text{C}(\text{Li})\text{CH}(\text{OEt})_2$

Ber 113 1290 (1978)

BSCF II 306 (1981)



$\text{LiCH}=\text{CHCR}$

TL 35 7643 (1994)

$\text{LiCH}=\text{CHCH}=\text{CHCH}_2\text{CH}(\text{OR})_2$ (R = Me, Et)

TL 30 7377 (1989)

$\text{LiCH}=\text{CHCH}=\text{CHCH}=\text{CHOEt}$

TL 30 7377 (1989)

$\text{LiC}(\text{Ts})=\text{CHCHROLi}$

JOC 54 1491 (1989)

$\text{H}_2\text{C}=\text{C}(\text{Li})\text{CHO}$

JOC 52 2625 (1987)

$\text{LiC}(\text{SPh})=\text{CHCONLi}_2$

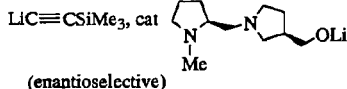
TL 30 2693 (1989)

$\text{EtO}_2\text{CCH}=\text{C}(\text{Li})\text{CO}_2\text{Et}$

TL 35 9101 (1994)

R³MTL 23 719 (1982)
JOC 57 6598 (1992)JOC 40 2250 (1975); 53 2214 (1988); 58
5482 (1993)
CC 363 (1981) (stereochemistry)
JACS 107 1034 (1985)
Org Syn Coll Vol 8 391 (1993)JACS 87 5632 (1965); 107 3915 (1985); 111 975,
989 (1989); 112 1897, 8189 (1990); 115 7944
(1993) (intramolecular); 117 8106 (1995)
JOC 38 3588 (1973); 50 2390 (1985); 52 3662, 3798,
4124 (1987); 58 3018 (1993) (intramolecular); 59
5305 (1994); 60 3550, 6173 (1995)
CL 447 (1979); 255 (1980) (both asymmetric)
TL 28 1019 (1987); 29 4217 (1988) (intramolecular);
31 4565 (1990); 34 7943 (1993); 36 4927 (1995
(intramolecular)

SL 683 (1993)

CL 929 (1982)
JOC 52 3491, 3662, 4191 (1987)
TL 34 4337, 7943 (1993); 36 1031, 1209 (1995)

Tetr 37 4111 (1981)



JOC 60 6046 (1995)



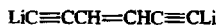
JOC 52 2332 (1987); 53 2214 (1988)



Syn Commun 12 977 (1982)

JOC 45 28 (1980); 52 3342 (1987)
Syn Commun 12 977 (1982)
JACS 115 3146 (1993)

TL 36 3687 (1995)



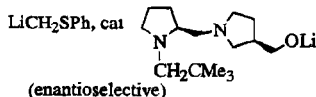
TL 29 4681 (1988) (mono and diol)



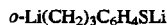
JOC 58 2966 (1993)





TL 32 2509 (1991)



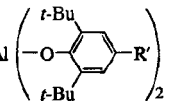

Tetr 37 4111 (1981)

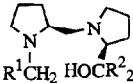
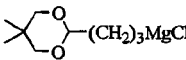


TL 36 4459 (1995)

$\text{LiCHRSO-}i\text{-Bu}$	JOC 54 2663 (1989) TL 33 127 (1992)
LiCHRSOAr	CL 289 (1977) JOC 45 4101, 5452 (1981) JCS Perkin I 1278 (1981) TL 31 5349 (1990)
LiCRXSOAr ($X = \text{F, Cl, Br}$)	TL 32 5599 (1991)
$\text{LiCHRSO}_2\text{Ar}$	JOC 54 3347, 4004 (1989); 60 3194 (1995) TL 32 1073, 1149, 4457 (1991); 35 6847 (1994) (intramolecular)
LiCR_2SeR	TL 31 67, 7419 (1990); 36 8115 (1995)
LiCH_2Cl	TL 25 835 (1984); 27 795 (1986) SL 491 (1994)
LiCHX_2 ($X = \text{Cl, Br, I}$)	JACS 96 3010 (1974); 104 4708 (1982); 106 3030 (1984); 108 3102 (1986) TL 22 3745 (1981) Topics Curr Chem 106 55 (1982) (review) JOC 53 863, 1227 (1988); 58 5493 (1993)
LiCFBr_2	SL 987 (1995)
LiCX_3 ($X = \text{Cl, Br}$)	JACS 96 3010 (1974) Topics Curr Chem 106 55 (1982) (review) JOC 55 1281 (1990)
LiCF_2CF_3	TL 26 5243 (1985) JOC 52 2481 (1987)
LiR_f	SL 91 (1993) (review)
	Ber 115 1990 (1982)
$\text{MCH}_2\text{CH}_2\text{SiMe}_3$ ($M = \text{Li, MgBr}$)	JOC 47 1983 (1982)
	TL 23 259 (1982) JACS 115 10754 (1993)
$\text{H}_2\text{C}=\text{C}(\text{Li})\text{SiMe}_3$	TL 23 259 (1982); 31 4937 (1990)
LiCOR	JOC 48 1144, 3367 (1983) TL 24 4907 (1983); 25 1651 (1984) JACS 110 957 (1988); 112 455 (1990)
LiCOAr	JOC 58 5843 (1993)
$\text{NaC}\equiv\text{CH}$	Org Syn Coll Vol 3 416 (1955) Syn 211 (1982)
$\text{NaC}\equiv\text{CR}$	JOC 38 3588 (1973)

R³M

- $\text{RC}\equiv\text{CH}$, NaOH (phase transfer) *Ann* 1750 (1982)
 NaCN *Org Syn Coll Vol* 2 7 (1943)
 NaCH_2NO_2 *Org Syn Coll Vol* 4 221 (1963)
 $\text{KC}\equiv\text{CR}$ *JACS* 110 6890 (1988); 113 3850 (1991); 114 2544 (1992); 115 7612 (1993) (all intramolecular)
TL 35 8655 (1994) (intramolecular)
 KCH_2NO_2 *Org Syn Coll Vol* 5 833 (1973)
 RMgX *Org Syn Coll Vol* 1 188 (1941); 3 200 (1955)
JACS 73 4462 (1951); 74 4954 (1952); 81 2748 (1959) (stereochemistry); 103 4540 (1981) (stereochemistry); 107 4573, 6411 (1985) (both stereochemistry)
 M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-Metallic Substances," Prentice Hall, Englewood Cliffs, New Jersey (1954) (review)
JOC 27 3860 (1962) (stereochemistry); 37 1918 (1972) (stereochemistry); 50 2179 (1985) (bicyclic ketones); 51 5353 (1986) (2-alkoxy aldehyde stereoselectivity); 54 4158 (1989); 57 5166 (1992)
BSCF 219 (1971) (stereochemistry)
TL 4383 (1979); 21 1031 (1980) (asymmetric); 23 5211 (1982) (δ -keto ester stereoselectivity); 28 2629 (1987); 35 4645 (1994); 36 8557, 8561 (1995)
JCS Perkin II 597 (1981) (stereochemistry)
JCS Perkin I 197 (stereochemistry using chiral alkoxide ligand), 979 (stereochemistry) (1982)
CC 1600 (1986) (α -alkoxy or -siloxy ketone diastereoselectivity)
SL 24 (1989)
 RMgX , crown ether *JACS* 107 6411 (1985) (stereochemistry)
 RMgX , *n*-Bu₄NBr *CC* 923 (1987) (Cram selective)
 MAD/RMgX *SL* 683 (1993)
 RMgX , MeAl  ($\text{R}' = \text{Me}, t\text{-Bu}$) *JACS* 107 4573 (1985); 110 3588 (1988) (aldehydes and cyclic ketones only, axial addition, anti-Cram)
TL 29 3101 (1988) ($\text{RCHO} \gg \text{R}_2\text{CO}$)
JOC 43 4094 (1978) (stereoselective)
 RMgOR' or RMgNR'_2 
 RMgX , $\text{HOCH}_2\text{CH}(\text{Ph})\text{CH}(\text{Ph})\text{OH}$ (enantioselective) *Angew Int* 31 84 (1992)


R_2Mg	JOC 37 1918 (1972) (stereochemistry) CL 601 (1978) (asymmetric) JACS 101 1455 (1979) (asymmetric); 107 6411 (1985) (stereochemistry); 114 1778 (1992) (α -alkoxy ketones); 117 5055 (1995) (α - and β -alkoxy aldehydes and ketones)
Me_2Mg , (LiClO ₄)	JOC 44 4371 (1979)
R_2Mg , chiral 	JACS 101 1455 (1979) Tetr 37 4111 (1981)
R_2Mg ; MOR (M = Li, Na, K), <i>n</i> -Bu ₄ NBr or (PhCH ₂ NEt ₃)Cl	JOC 55 3281 (1990)
Me_3SiCH_2MgCl	TL 23 3249 (1982) Ber 115 1132 (1982)
$PhMe_2SiCH_2MgCl$	TL 30 229 (1988)
(<i>i</i> -PrO) Me_2SiCH_2MgCl	TL 25 4245 (1984) Org Syn Coll Vol 8 315 (1993)
$PhSCH_2SiMe_2CH_2MgCl$	SL 1069 (1995)
$CH_3CH(OR)CH_2CH(CH_3)MgX$	TL 33 305 (1992)
$(RO)_2CHCHRCH_2MgX$	TL 30 3547 (1989)
 $(CH_2)_3MgCl$	JOC 57 4560 (1992)
$XMgCX_2CO_2R$	JCS Perkin I 2063 (1982) BSCF II 230 (1983)
$R_2C=CRMgX$	JOC 52 3798 (1987); 56 417 (1991) SL 24 (1989) JACS 113 5365 (1991); 114 3983 (1992)
$H_2C=CHCH=CHMgBr$	JOC 52 4416 (1987)
$H_2C=CHC(=CH_2)MgCl$	JOC 44 4788 (1979)
$HC\equiv CMgX$	TL 34 7943 (1993)
$RC\equiv CMgBr$	TL 28 1019 (1987) JACS 112 8189 (1990) JOC 60 6173 (1995)
$Me_3SiC\equiv CMgBr$	TL 34 4337 (1993)
$XMgOCH_2C\equiv CMgX$	JOC 58 3692 (1993)
$BrMgC\equiv CMgBr$	CC 363 (1981) (alkanone to alkynol) JOC 58 7149 (1993) (alkanal to alkynediol)
$HC\equiv CC\equiv CMgX$	TL 34 1803, 2835 (1993) SL 1135 (1995)

R^3M

RCaX

JOMC 66 219 (1974)

JOC 55 5045 (1990)

 $RCH=CRB$ 

JOC 42 579 (1977)


TL 31 4545 (1990); 36 987 (1995)

 $RCH=CHBCy_2$, R_2Zn , chiral amino alcohol
(enantioselective)

Helv 75 170 (1992)

JACS 115 1593 (1993) (intramolecular)

TL 36 2607 (1995) (intramolecular)

 $RC\equiv CBMe_2$, cat  BR' ($R' = Me, n-Bu$,
Ph; enantioselective)

JACS 116 3151 (1994)

 $Me_3SiC\equiv CB$ 

JOC 57 2941 (1992)

 R_nAlX_{3-n} ($X = \text{halogen, OR, NR}_2$)

JOC 44 4792 (1979)

 $RAlCl_2$ TL 33 4579 (1992) (α -formyl amides) R_3Al

JOC 37 1918 (1972); 40 1469 (1975)

BCSJ 47 1971 (1974)

Chem Pharm Bull 35 2605 (1987)

TL 29 753 (1988); 33 4353 (1992) (β -keto amides
and esters); 35 1393 (1994)

JACS 111 6666 (1989)

 $Me_3Al, MgBr_2$

JACS 111 6682 (1989)

 $Me_3Al, ZnBr_2$

TL 36 3737 (1995) (2-sulfinyl-1-alkanone)

 $t-Bu_2AlCH=CHR$

JOC 53 4395 (1988)

 $RC\equiv CAIR_2$

Compt Rend 261 1992 (1965)

BSCF 205 (1968)

Chem Pharm Bull 35 2605 (1987)

JACS 112 4552 (1990)

 $(RC\equiv C)_3Al$

Compt Rend C 262 289 (1966)

 $NaAlEt_2(C\equiv CR)_2$

JOC 60 6173 (1995)

 $LiAlR_4$

JOC 39 3258 (1974); 47 693 (1982)

TL 26 4181 (1985) (on menthyl phenylglyoxalate)

 $Me_4AlMgBr$

TL 29 3769 (1988)

 Me_4TiLi (enone or $ArCOR > satd RCOR$)

JACS 116 371 (1994)

 CF_3SiMe_3 , cat Et_4NF

TL 34 8241 (1993)

 CF_3SiMe_3 , cat $n-Bu_4NF$

JACS 111 393 (1989)

JOC 56 984, 5143 (1991)

CC 796 (1991)

SL 643 (1991)

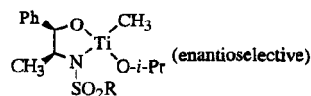
 CF_3SiMe_3 , cat chiral R_4NF (enantioselective)

TL 35 3137 (1994)

CF_3SiMe_3 , KF	JOC 57 1124 (1992)
$\text{RCF}_2\text{SiMe}_3$, KF	SL 717 (1995)
R_3SiMe_3 , cat <i>n</i> -Bu ₄ NF	JOC 56 984 (1991)
RSiR'_3 , cat $[(\text{Me}_2\text{N})_3\text{S}]\text{Me}_3\text{SiF}_2$ ($\text{R} = \text{CHCl}_2$, CCl_3 , CCl_2Me , $\text{CF}_2\text{CH}=\text{CH}_2$, $\text{CF}=\text{CF}_2$, $\text{CF}=\text{CF-}n\text{-Bu}$, $\text{CF}=\text{CFSei}$, $\text{CCl}=\text{CF}_2$, $\text{CF}=\text{CHF}$)	JACS 107 4085 (1985)
ArCH(OR)SiMe_3 , CsF	JOC 56 5213 (1991)
$(\text{Me}_3\text{SiCH}_2)_2\text{S}$, <i>n</i> -Bu ₄ NF ($\text{R}^3 = \text{CH}_2\text{SMe}$)	SL 557 (1991)
$\text{PhSCH}_2\text{SiMe}_3$, cat <i>n</i> -Bu ₄ NF	TL 29 3319 (1988)
RSCRPhSiR_3 , CsF	TL 32 815 (1991)
$\text{HC}\equiv\text{CCH}_2\text{SiMe}_3$, <i>n</i> -Bu ₄ NF (allenic product)	TL 22 455 (1981)
$\text{ArCH}_2\text{SiMe}_3$, <i>n</i> -Bu ₄ NF	TL 24 4217 (1983) BSCF II 90 (1985) JOC 52 4381 (1987); 54 4372 (1989)
RSiMe_3 ($\text{R} = \text{benzylic}$, 4-picolyl, phenylallyl), KF-18-crown-6 or <i>n</i> -Bu ₄ NF-silica	TL 23 577 (1982)
RSiMe_3 ($\text{R} = \text{benzyl}$, allyl, heterocyclic); CsF or <i>n</i> -Bu ₄ NF-silica	TL 5079 (1982)
$\text{ArCONRCH}_2\text{SiMe}_3$, CsF	TL 30 5837 (1989)
ArSiMe_3 , cat KO- <i>t</i> -Bu	Angew Int 20 265 (1981)
ArSiMe_3 , CsF	TL 28 2933 (1987) (intramolecular)
$(\text{OC})_3\text{Cr}\cdot\text{ArSiMe}_3$, cat CsF	Angew Int 20 266 (1981)
$\text{RCH}=\text{CHSiMe}_3$, $\text{BF}_3\cdot\text{OEt}_2$	JOC 56 5010 (1991); 58 4823 (1993) (both intramolecular)
$\text{RCH}=\text{CHSiMe}_3$, SnCl_4	JOC 56 5010 (1991); 58 4823 (1993) (both intramolecular)
$\text{RCH}=\text{CHSiMe}_3$, TiCl_4	JOC 56 4337 (1991)
$\text{RCH}=\text{C}(\text{SiMe}_3)\text{CO}_2\text{R}$, <i>n</i> -Bu ₄ NF ($\text{R}^3 = \text{RCH}=\text{CCO}_2\text{R}$)	Syn 734 (1986)
$\text{H}_2\text{C}=\text{C}(\text{SiMe}_3)\text{SOAr}$, cat <i>n</i> -Bu ₄ NF ($\text{R}^3 = \text{H}_2\text{C}=\text{CSOAr}$)	TL 31 673 (1990)
$\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, AlCl_3	TL 2449 (1976) (silylalkynol)
$\text{Me}_3\text{SiC}\equiv\text{CSiMe}_3$, KF, 18-crown-6	CC 840 (1979) (silylalkynol and alkynediol)
$\text{RC}\equiv\text{CSiMe}_3$, CsF	SL 482 (1994) (intramolecular) TL 36 209 (1995) (intramolecular)

R³M

RC≡CSiMe ₃ , <i>n</i> -Bu ₄ NF	Angew Int 15 498 (1976) Tetr 39 975 (1983) SL 38 (1995) (intramolecular)
RC≡CSiMe ₃ , cat (Ph ₄ P)HF ₂	SL 1033 (1995)
PhCOSiMe ₃ , <i>n</i> -Bu ₄ NF/H ₂ O (R ³ = PhCO)	TL 22 1881 (1981)
R ₂ SnX ₂ I (X = F, Cl)	CL 1337 (1981)
<i>n</i> -Bu ₃ SnCH ₂ CH ₂ COX (X = OMe, NHPH), TiCl ₄	JOC 50 5907 (1985)
Me ₃ SnR; EtAlCl ₂ , Et ₂ AlCl or TiCl ₄	TL 30 1473 (1989) (intramolecular)
RCH(OR)Sn(<i>n</i> -Bu) ₃ , TiCl ₄	JACS 112 6118 (1990)
RC≡CSnEt ₃ , ZnCl ₂	TL 495 (1967)
RC≡CSn(<i>n</i> -Bu) ₃ , TiCl ₄	CC 102 (1986)
R ₄ Pb, TiCl ₄	JACS 109 4395 (1987) (aldehydes only)
RCH(OR)Pb(<i>n</i> -Bu) ₃ , BF ₃ ·OEt ₂ or TiCl ₄	JACS 112 6118 (1990) JOC 57 2981 (1992)
R ₄ SbCH ₂ X (X = Ph, CH=CH ₂ , CH=CHCO ₂ Et, CO ₂ R, CN)	JOC 56 1381 (1991) (aldehydes only)
<i>n</i> -BuToCH=CHCH=CH ₂ , <i>n</i> -BuLi	TL 36 3539 (1995)
RC≡CYCl ₂	JACS 112 8189 (1990)
RTi review	Topics Curr Chem 106 1 (1982)
RTiCl ₃	Angew Int 19 1011 (1980); 22 989 (1983) Syn Commun 11 647 (1981) JACS 105 4833 (1983) CC 1600 (1986) (α-alkoxy or -siloxy ketone diastereoselectivity) Tetr 42 2931 (1986) TL 33 4579 (1992) (α-formyl amides) SL 351 (1995)
TiCl ₄ , Mg, BrCH ₂ CH ₂ Br	TL 29 1583 (1988) (forms 1,4-diol)
RO ₂ CCH ₂ CH ₂ TiCl ₃	JACS 99 7360 (1977); 105 651 (1983); 108 3745 (1986)
RO ₂ CCH ₂ CH ₂ TiCl ₃ , Ti(O- <i>i</i> -Pr) ₄	JACS 107 2138 (1985); 108 3745 (1986)
RO ₂ CCH ₂ CH ₂ TiCl ₃ (O- <i>i</i> -Pr) _{3-x} (x = 0-3)	TL 32 1867 (1991)
XCOCH ₂ CH ₂ TiCl ₂ (O- <i>i</i> -Pr) (X = OR, NHR)	TL 32 233 (1991)
XCOCH ₂ TiCl(O- <i>i</i> -Pr) ₂ (X = OR, NR ₂)	TL 33 6599 (1992)
R ₂ TiCl ₂	Angew Int 19 1011 (1980) Ber 118 1441 (1985)


 $\text{RTi}(\text{OR}')_3$

TL 27 5711 (1986)

Angew Int 19 1011 (1980); 21 135 (1982); 22 31 (1983)

Helv 63 2451 (1980); 64 357, 2485 (1981); 65 249 (1982)

JACS 105 4833 (1983); 107 4577 (1985)

Ber 118 1421, 1441 (1985)

JOC 50 422 (1985)

 CC 1600 (1986) (α -alkoxy or -siloxy ketone diastereoselectivity)

Tetr 42 2931 (1986)

 TL 27 5351 (1986) (β -Me₂N ketone); 28 2959 (1987); 32 903 (1991)

SL 503 (1992)

Org Syn Coll Vol 8 495 (1993)

 $\text{MAD}/\text{RTi}(\text{O}-i\text{-Pr})_3$

SL 683 (1993)

 $\text{RCH}=\text{CRTi}(\text{O}-i\text{-Pr})_3$

TL 30 3271 (1989)

 $\text{RC}\equiv\text{CTi}(\text{O}-i\text{-Pr})_3, \text{TiCl}_4$

JOC 58 2468 (1993)

 $\text{R}_2\text{Ti}(\text{OR}')_2$

Angew 21 135 (1982)

Ber 118 1421 (1985)

TL 35 2849 (1994)

 $(\text{NCCCH}_2\text{CH}_2)_2\text{Ti}(\text{O}-i\text{-Pr})_2$

TL 29 2395 (1988)

 Me_4Ti

Angew 21 135 (1982)

Ber 118 1421 (1985)

 $\text{RZr}(\text{OR}')_3$

Helv 64 1552 (1981)

Angew Int 21 135 (1982); 22 31 (1983)

 Me_4Zr

Angew Int 21 135 (1982)

TL 31 51 (1990)

JOC 56 3988 (1991)

 $\text{Cp}_2\text{ZrMe}_2, \text{KO}-t\text{-Bu}$

TL 32 5893 (1991)

 Cp_2ZrRCl (R = 1° alkyl, vinylic), cat AgClO_4

TL 33 5965 (1992)

 Cp_2ZrRCl (R = 1° alkyl, vinylic), cat ZnBr_2

JOC 60 3278 (1995)

 MeHX_3 (X = Cl, OEt)

 TL 27 5351 (1986) (α -hydroxy ketone)

 Me_2VOCl

 TL 27 5351 (1986) (β -hydroxy ketone)

 $\text{Me}_2\text{Nb}(\text{OEt})_3$

 TL 23 2301 (1982) ($\text{RCHO} > \text{R}_2\text{CO}$)

 MeNbCl_4

 TL 23 2301 (1982) ($\text{RCHO} > \text{R}_2\text{CO}$)

 $\text{Me}_2\text{Ta}(\text{OEt})_3$

 TL 23 2301 (1982) ($\text{RCHO} > \text{R}_2\text{CO}$)

 $\text{MeTa}(\text{OEt})_4$

 TL 23 2301 (1982) ($\text{RCHO} > \text{R}_2\text{CO}$)

 MeTaCl_4

 TL 23 2301 (1982) ($\text{RCHO} > \text{R}_2\text{CO}$)

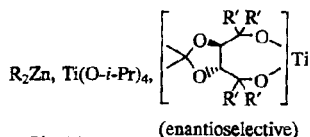
R³M

MeCrCl	TL 27 5351 (1986) (β -hydroxy ketone)
MeCrCl ₂	TL 27 5355 (1986) (RCHO and β -Me ₂ N ketone)
MeMnCl	TL 27 5351 (1986) (α - and β -Me ₂ N ketone)
RMnX	TL 3383 (1977); 27 4445 (1986) (RCHO > R ₂ CO); 33 4353 (β -keto amide), 6963 (RCHO > R ₂ CO) (1992); 35 1969 (1994)
(Cl ₂ CH) ₃ MnLi	TL 27 5351 (1986) (α -Me ₂ N ketone)
Me ₂ Fe	TL 31 507 (1990) (RCHO > R ₂ CO)
Me ₃ FeLi	TL 31 507 (1990) (RCHO > R ₂ CO)
Me ₃ FeMgBr	TL 31 507 (1990) (RCHO > R ₂ CO)
Me ₃ CoLi	TL 31 511 (1990) (RCHO > R ₂ CO)
RCu·MgBr ₂	JOC 50 422 (1985) TL 34 7075 (1993)
RCu·BF ₃	JOC 47 119 (1982)
R ₂ CuLi	JOC 31 3128 (1966); 40 1460 (1975); 50 422 (1985); 60 7870 (1995) CC 320 (1973) TL 3128 (1974); 21 1035 (1980) (asymmetric); 27 3059, 5351 (β -Me ₂ N ketone) (1986); 34 6399, 6689 (1993); 35 1969 (1994) JACS 107 6411 (1985) (stereoselectivity); 111 1351 (1989) Tetr 44 6889 (1988) SL 24 (1989)
(H ₂ C=CMe) ₂ CuLi	TL 28 4147 (1987)
(CH ₃ CH=CH) ₂ CuLi·n-Bu ₃ P	JOC 55 863 (1990)
[H ₂ C=C(SiMe ₃) ₂] ₂ CuLi·n-Bu ₃ P	TL 32 857 (1991); 35 6639 (1994)
R ₂ CuLi, crown ether	JACS 107 6411 (1985) (anti-Cram)
R ₂ CuLi, n-Bu ₄ NBr	CC 923 (1987) (anti-Cram)
R ₂ CuLi, BF ₃ ·OEt ₂	JACS 111 1351 (1989)
R ₂ CuLi, R ₃ SiCl	TL 30 1975 (1989); 34 6689 (1993) SL 309 (1992)
R ₂ CuLi, Me ₃ SiCN	TL 34 6689 (1993)
Me ₃ SiH/R ₂ CuLi/H ₂ O	Syn Commun 13 213 (1983)
[MeO ₂ CC(=CH ₂)CuC≡C(CH ₂) ₃ CH ₃] ₂ Li	TL 3897 (1975)
(ThCuR)Li, Me ₃ SiX (X = Cl, CN)	TL 34 6689 (1993)
R ₃ CuLi ₂	JACS 97 5280 (1975) (stereochemistry)

	TL 2659 (1976) (stereochemistry); 1709 (1977) (stereochemistry); 28 5547 (1987) JOC 54 4158 (1989)
$(RC\equiv C)_3CuLi_2$	CC 892 (1975) (on enones)
R_3Cu_2Li , $BF_3 \cdot OEt_2$	JACS 111 1351 (1989)
$R_5Cu_3Li_2$, crown ether	JACS 107 6411 (1985) (anti-Cram)
$Me_2Cu(CN)Li_2$	JACS 106 6414 (1984) (on RCHO)
$R_2Cu(CN)Li_2$, crown ether	JACS 107 6411 (1985) (anti-Cram)
$ArCH_2Cu(CN)ZnX$	JOC 53 5789 (1988)
$PhSCHRCu(CN)ZnCl$	TL 31 7575 (1990)
$RCu(CN)ZnI$, $BF_3 \cdot OEt_2$ (RCHO only)	TL 29 3887 (1988); 31 1833 (1990); 32 4909 (1990) JOC 56 5974 (1991)
$RCO_2CH_2Cu(CN)ZnX$, $BF_3 \cdot OEt_2$ (RCHO only)	JOC 54 5202 (1989); 58 588 (1993)
$ArCH_2Cu \cdot ZnI_2$, $BF_3 \cdot OEt_2$	JOC 58 2694 (1993)
$RZnX$	"Methods of Elemento-organic Chemistry," Vol 3, North-Holland, Amsterdam (1967) (review) Adv Organometal Chem 12 83 (1974) (review) TL 29 2175 (1988); 32 3417 (1991); 36 4439 (1995)
CF_3CX_2ZnX ($X = Cl, Br$)	TL 27 2135, 2139 (1986)
$RC\equiv CZnX$	JOC 59 5865 (1994)
EtO_2CCF_2ZnBr	TL 32 7255 (1991)
$RO_2CCHRZnX$	See page 1130 under Zn.
$(RO_2CCHRCH_2)_2Zn$, Me_3SiCl	JACS 109 8056 (1987)
$BrZnCH_2CR=CHCO_2SiMe_3$	JOMC 219 C1 (1981) (α or γ)
Me_2Zn	TL 31 5479 (1990)
$ArCH_2ZnX$, Me_3SiCl	TL 35 5637 (1994)
$RZnR'$	TL 35 5587 (1994)
$RO_2C(CH_2)_nZnI$ ($n = 1-4$), $(i-PrO)_3TiCl$	JOC 53 1343 (1988)
$PhCO(CH_2)_nZnI$ ($n = 3, 6$), $(i-PrO)_3TiCl$	JOC 53 1343 (1988)
$t-BuSOCHRZnX$	JOC 54 2663 (1989)
R_2Zn (enantioselective)	Chem Rev 92 833 (1992) (review)
R_2Zn , $BF_3 \cdot OEt_2$	Tetr 44 6889 (1988)
R_2Zn , $TiCl_4$	Syn Commun 11 261 (1981) Angew Int 22 989 (1983) JACS 105 4833 (1983) JOC 52 320 (1987) Tetr 44 6889 (1988)

R³M R_2Zn , $Ti(OCHEtPh)_4$ (enantioselective)

JACS 111 7265 (1989)

 $R' = Ph$

Angew Int 30 99 (1991)

Tetr 48 5719 (1992)

JOC 60 3936 (1995)

SL 1043 (1995)

 $R' = \text{aryl}$

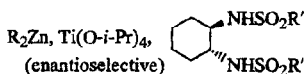
Angew Int 30 1321 (1991)

 $R' = \beta\text{-naphthyl}$

Tetr 48 5719 (1992)

 R_2Zn , $Ti(O-i-Pr)_4$, cat $RSO_2NHCHMeCHR'OH$, cat CaH_2 (enantioselective)

SL 573 (1992)



TL 30 1657, 7095 (1989); 34 3115, 5261, 5881

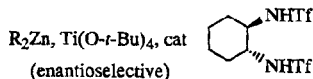
(1993); 35 4539, 5849, 9007 (1994); 36 231, 1023, 4947 (1995)

JOC 57 1956 (1992); 59 3760, 4143 (1994); 60 3311 (1995)

Tetr 48 5691 (1992)

Angew Int 32 582 (1993)

SL 410 (1994)



TL 35 4539 (1994)

 R_2Zn , cat bis[(-)-camphorquinone- α -dioximato] cobalt(II) or palladium(II)] (enantioselective)

CL 841 (1983) (ArCHO only)

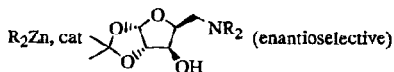
 R_2Zn , cat cinchona alkaloids (enantioselective)

JOC 52 135 (1987) (ArCHO only)

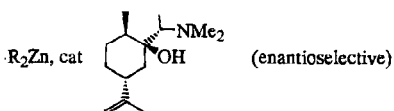
TL 28 6163 (1987); 30 6427 (1989)

 R_2Zn , cat Chirald (enantioselective)

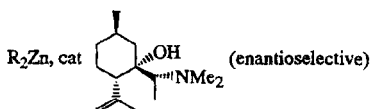
TL 35 5587 (1994)



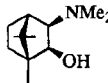

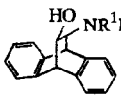
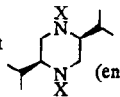
TL 35 4115 (1994)



JOC 57 7175 (1992)



JOC 59 1730 (1994)

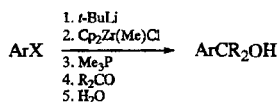
- R_2Zn ,  (enantioselective) JACS 108 6071 (1986) (RCHO only); 111 4028 (1989) (mechanism); 117 4382 (1995)
 TL 30 6427 (1989)
- R_2Zn ,  [X = CH₂NMe(CH₂)₂NMe₂, CON(*i*-Pr)₂, CH₂N(*i*-Pr)₂] (enantioselective) TL 29 5645 (1988) (RCHO only)
- R_2Zn , cat  (R¹ = R² = Me; R¹ = H, R² = OTf) (enantioselective) TL 33 3147 (1992)
- R_2Zn , cat  (X = H, Li) (enantioselective) TL 28 4841 (1987) (ArCHO only)
- R_2Zn , cat PhCHOHCHMeNR₂ (enantioselective) CC 1690 (1987)
 TL 28 3013 (1987) (ArCHO only); 30 6427 (1989); 31 5185 (1990)
 JOC 56 4264 (1991); 59 7908 (1994)
 JACS 114 2260 (1992); 115 4497 (1993)
- R_2Zn , cat (CO)₃Cr-PhCHOHCHMeNR₂ (enantioselective) TL 33 1693 (1992)
- R_2Zn , cat (CO)₃Cr-areneaminoalcohol (enantioselective) JOC 58 1238 (1993)
 SL 367 (1993)
- R_2Zn , cat Me₃CCHOHCH₂NR₂ (enantioselective) JACS 110 7877 (1988) (RCHO only)
- R_2Zn , cat PhCHOHCHMeNMeCH₂-polymer (enantioselective) JOC 53 927 (1988)
- R_2Zn , cat PhCHOHCHMeNMe-silica or alumina (enantioselective) JOC 55 4832 (1990)
- R_2Zn , cat Ph₂C(OH)CH(NH₂)CH₂C₆H₄O-polymer (enantioselective) JOC 55 304 (1990)
- R_2Zn , chiral polymeric amino alcohol (enantioselective) JOC 52 4140 (1987) (ArCHO only)
- R_2Zn , several chiral amino alcohols (enantioselective) TL 25 2823 (1984) (PhCHO only); 28 6163 (1987) (ArCHO only); 30 6427 (1989)
- R_2Zn , chiral ferrocenylamino alcohols (enantioselective) JOC 56 2218 (1991); 57 742 (1992)
 SL 1050 (1995)
- R_2Zn , chiral piperiziny alcohol (enantioselective) JOC 56 3063 (1991)
- R_2Zn , chiral pyrrolidinylmethanols (enantioselective) CC 467 (1987)
 JACS 109 7111 (1987)
 TL 30 6427 (1989)
 JOC 59 1160 (1994); 60 7712 (1995)

$(\text{RCH}=\text{CR})_2\text{Zn}$	TL 32 2449 (1991)
$\text{RCH}=\text{CHZnEt}$	JOC 60 2660 (1995)
$\text{RC}\equiv\text{CZnX}$	TL 28 1019 (1987)
$\text{RC}\equiv\text{CZnBr}$, LiOCHPhCHMeNMe_2 (enantioselective)	SL 547 (1990)
R_3ZnMgX	SL 175 (1994)
$(\text{ArCH}_2)_2\text{Cd}$, MgX_2	TL 1581 (1979)
$\text{MeLa}(\text{OTf})_2$	JOC 55 3565 (1990)
CeCl_3 or cat CeCl_3/RLi or RMgX	TL 35 6713 (1994)
RCeX_2 ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl)	CC 1042 (1982) TL 25 4233 (1984); 27 3329 (1986); 29 3171 (1988); 33 293, 4759, 6963 (1992); 35 285, 1157, 8453 (1994) JOC 49 3904 (1984); 57 1646 (1992); 60 202, 2022 (1995) JACS 111 4392 (1989); 112 291, 9272 (1990); 115 3146 (1993)
$\text{Cl}_2\text{CHCeCl}_2$	JOC 53 4143 (1988) JACS 112 3475 (1990) TL 35 3485 (1994)
$\text{Me}_3\text{SiCH}_2\text{CeCl}_2$	JOC 52 281 (1987)
$\text{PhSO}_2\text{CR}_2\text{CeCl}_2$	TL 32 4457 (1991)
$\text{NCCH}_2\text{CeCl}_2$	TL 32 5473 (1991); 33 6963 (1992)
RCeCl_2 ($\text{R} = \text{vinyl}$)	TL 25 4233 (1984); 29 6541 (1988); 31 4547 (1990); 32 2787 (1991) JACS 108 7873 (1986); 110 879 (1988); 111 4392 (1989); 112 277, 5562, 9284 (1990); 113 1335 (1991); 116 506, 7658 (1994) JOC 54 2278, 2291 (1989); 55 1589 (1990); 56 912, 6538 (1991); 57 1646, 3956 (1992); 58 4952, 6874 (1993); 59 2033 (1994)
$\text{RC}\equiv\text{CCeCl}_2$	CL 1543 (1984) TL 25 4233 (1984); 26 1549 (1985); 27 195 (1986); 28 3971, 4583 (1987); 29 2923, 6951 (1988); 32 1707 (1991); 36 1031, 1733 (1995) CC 1290, 1474 (1987) JOC 52 4135 (1987); 53 2972 (1988); 57 1646 (1992); 58 4662 (1993); 59 6922 (1994); 60 3550 (1995) JACS 111 9130 (1989); 113 694 (1991) (intra- molecular); 116 10310 (1994) (intramolecular)
$(\text{RC}\equiv\text{C})_2\text{CeCl}$	TL 36 1031 (1995)

R³M

(RC≡C) ₃ Ce	CL 1543 (1984)
ArCeCl ₂	CC 1042 (1982) JOC 49 3904 (1984); 53 4978 (1988); 57 7118 (1992); 59 3165 (1994) JACS 111 4392 (1989) TL 31 6721 (1990); 33 293 (1992); 35 285, 8453 (1994)
RCe(BINOL) (R = Me, <i>n</i> -Bu, Ph)	TL 35 285 (1994) (diastereoselective)
RCe(<i>O</i> - <i>i</i> -Pr) ₃ MgX	TL 33 6963 (1992) (RCHO > R ₂ CO)
RSmI ₂ , Me ₃ SiCl, HMPA	JOC 58 3455 (1993)
PhCH ₂ OCH ₂ C(=NAr)SmI ₂	JACS 112 2437 (1990)
Cp ₂ SmRX	SL 733 (1992)
RYbI	JOC 52 3524 (1987)
RC≡CYbCl ₂	JACS 112 8189 (1990)
RYb(OTf) ₂ (R = 1°, 3° alkyl; aryl; vinylic)	JOC 55 4990 (1990)
RU[N(SiMe ₃) ₂] ₃	JOC 53 1034 (1988)

For addition reactions involving vinylic copper reagents derived from organocopper additions to alkynes, see page 452, Section 2.28.



TL 31 5563 (1991)



See also the direct reaction of aldehydes and ketones with allylic halides and other allylic substrates plus metals earlier in this section, as well as page 236, Sections 7 and 8, for ene-type reactions.

Reviews:

JOMC 69 1 (1974) (Li, Na, Mg, Zn, Cd, Al); 285 31 (1985)

Heterocycles 18 357 (1982)

Angew Int 21 555 (1982) (diastereoselectivity)

Topics Curr Chem 106 55 (1982) (Ti)

SL 1 (1989) (allylic silanes)

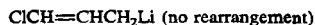
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 1.1, p 1

Chem Rev 93 2207 (1993)

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21b, G. Thieme, Stuttgart-New York (1995), pp 1357-1602

allylic organometallic

allylic lithium compounds

 Tetr 42 2803 (1986)
 JACS 113 5893 (1991)

 JOMC 236 139 (1982)
 SL 769 (1990)
 TL 34 3145 (1993)

 CL 713 (1979)
 TL 33 7997 (1992)

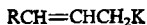

CC 1326 (1982)



JACS 113 910 (1991)



JOC 59 6018 (1994)


 CL 1331 (1982)
 TL 36 607 (1995)


JOC 54 5198 (1989)


 TL 3829 (1975); 21 365 (1980); 26 823 (1985); 28
 869 (1987); 31 1803 (1990); 35 6101 (1994); 36
 8557 (1995)
 Austral J Chem 37 65 (1984)
 JOC 51 3290 (1986); 53 1010 (1988); 54 5198, 6129
 (1989); 58 2686 (1993)
 SL 24 (1989)
 JACS 113 5402 (1991); 114 6910 (1992)


JOC 52 1603 (1987)



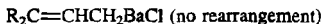
BSCF 4038 (1969)



SL 788 (1993)



TL 27 4961 (1986)



JACS 113 8955 (1991); 116 6130 (1994)



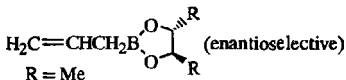
SL 788 (1993)

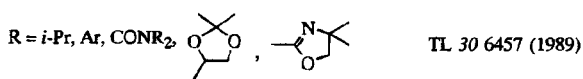


JOC 55 1868 (1990)

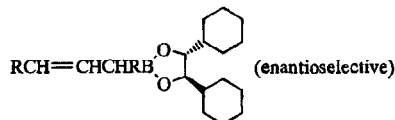

 JOC 46 1309 (1981); 55 1868 (1990); 60 4838
 (1995) (α -amido ketones)

 TL 32 1945 (α -hydroxy ketones), 4619 (α -keto
 acids), 5677 (α -keto acids) (1991); 34 7071 (1993)

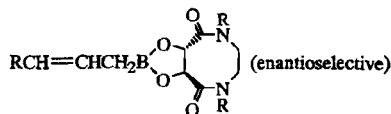
 TL 28 4169 (1987)
 JOC 55 1868 (1990)

 JACS 107 8186 (1985)
 TL 30 6457 (1989)
 JOC 55 1868 (1990)



TL 30 6457 (1989)



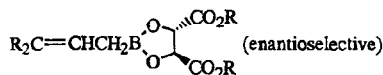
TL 35 4751 (1994)

 $R = CF_3, C_6H_{11}$

JOC 60 3806 (1995)

 $R = CH_2Ph$

JACS 110 3979 (1988); 112 6348 (1990)

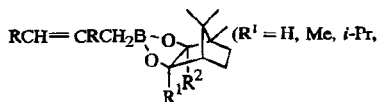


JACS 107 8186 (1985); 108 294 (1986); 109 953, 8117 (1987); 111 2967 (1989); 112 6339, 6348 (1990); 115 2268 (1993)

TL 26 4327 (1985); 27 3349 (1986); 28 931 (1987); 29 3541, 5579 (1988); 30 6457 (1989); 31 4707 (1990); 32 6285 (1991); 34 1351, 5421, 5931 (1993); 35 3405 (1994)

JOC 52 316 (1987); 54 915 (1989); 55 1143, 1868, 4109, 4117, 5938 (1990); 57 1637 (1992); 59 3347 (1994); 60 798, 5048 (1995)

SL 535, 927 (1993)

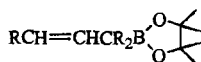


Angew Int 17 768 (1978); 19 218 (1980)

TL 4653 (1979)

Ber 114 359, 375, 2786, 2802 (1981); 115 2357 (1982)

$PhCH_2, Ph$; $R^2 = H, Me, PhCH_2, Ph$; enantioselective)



Angew Int 18 306 (1979)

JOMC 195 137 (1980)

JOC 49 3429 (1984); 53 5023 (1988); 55 1868 (1990); 60 798 (1995)

JACS 107 8186 (1985); 108 3422 (1986); 112 6348 (1990)

TL 28 869 (1989)

Ber 122 1777 (1989)



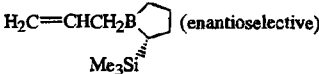
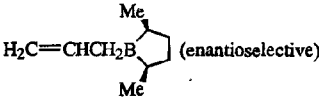
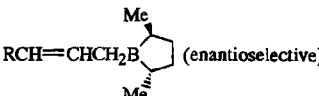
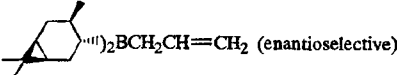
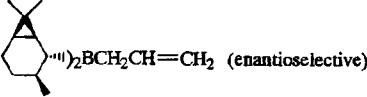
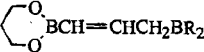

TL 28 4169 (1987); 30 3789 (1989)

JOC 55 1868 (1990)

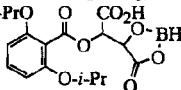


JOC 55 1868 (1990)

$\text{H}_2\text{C}=\text{CHCH}_2\text{B} \begin{array}{c} \text{O} \diagup \text{CH}_3 \\ \\ \text{O} \diagdown \text{CH}_3 \end{array} \quad (\text{enantioselective})$	JACS 107 8186 (1985)
$\text{RCH}=\text{CHCHClB}(\text{OR})_2$	Angew Int 23 437 (1984); 25 189 (1986) SL 759 (1990) (chiral) TL 34 1115 (1993)
$\text{H}_2\text{C}=\text{CHCHXB}(\text{OR})_2 \quad (\text{X} = \text{Cl}, \text{Br}, \text{OMe}, \text{SR})$	TL 24 3209 (1983)
$\text{RCH}=\text{CHCH}(\text{OMe})\text{B}(\text{OR})_2$	TL 28 5303 (1987)
$\text{H}_2\text{C}=\text{CHCH}(\text{SiMe}_3)\text{B}(\text{OR})_2$	Organomet 2 236 (1983)
$\text{H}_2\text{C}=\text{C}(\text{Br})\text{CH}_2\text{B}(\text{OPh})_2$	TL 32 6749 (1991)
$\text{H}_2\text{C}=\text{C}(\text{Br})\text{CH}_2\text{B} \begin{array}{c} \text{O} \diagup \text{CO}_2\text{R} \\ \\ \text{O} \diagdown \text{CO}_2\text{R} \end{array} \quad (\text{enantioselective})$	SL 639 (1994)
$\text{H}_2\text{C}=\text{C}(\text{CO}_2\text{Me})\text{CH}_2\text{B}(\text{OR})_2$	TL 34 6899 (1993)
$\text{ROCH}=\text{CHCH}_2\text{B}(\text{OR})_2$	TL 23 845 (1982); 24 2227 (1983); 27 3353 (1986); 36 1431 (1995) (intramolecular) JOC 47 2498 (1982); 53 5023 (1988); 54 915 (1989) Syn Commun 12 779 (1982) JACS 108 3422 (1986); 109 7575 (1987); 111 2984 (1989)
$\text{RSCH}=\text{CHCH}_2\text{B}(\text{OR})_2$	TL 21 4883 (1980)
$\text{Me}_3\text{SiCH}=\text{CHCH}_2\text{B}(\text{OR})_2$	TL 22 2751 (1981); 36 1581 (1995) (chiral)
$\text{ROSiMe}_2\text{CH}=\text{CHCH}_2\text{B}(\text{OR})_2$	TL 31 7563 (1990) (chiral)
$\text{ArSiMe}_2\text{CH}=\text{CHCH}_2\text{B}(\text{OR})_2$	TL 31 7563 (1990); 34 5421 (1993); 36 501 (1995) (all chiral)
$\text{H}_2\text{C}=\text{CHCH}_2\text{B} \begin{array}{c} \text{O} \\ \\ \text{N} \\ \\ \text{R} \end{array} \quad (\text{R} = \text{Me}, \text{Ph}, \text{Ts})$	JOC 55 1868 (1990)
$\text{H}_2\text{C}=\text{CXCH}_2\text{B} \begin{array}{c} \text{SO}_2\text{Ar} \\ \\ \text{N} \diagup \text{Ph} \\ \\ \text{N} \diagdown \text{Ph} \\ \\ \text{SO}_2\text{Ar} \end{array} \quad (\text{enantioselective})$	JACS 111 5495 (1989) (X = H, Cl, Br) TL 30 5235 (1989) (X = OAc); 31 3715 (1990) (X = H, Cl)
$\text{RCH}=\text{CHCHRBROH}$	JACS 104 2330 (1982)
$\text{RCH}=\text{CRCHRBET}_2$	CL 993 (1980) TL 27 5135 (1986)
$\text{RCH}=\text{CHCHRB}(\text{n-Bu})_2$	CL 993 (1980)
$\text{RCH}=\text{CRCHRB} \begin{array}{c} \text{O} \\ \\ \text{O} \end{array}$	JOC 42 2292 (1977); 51 886 (1986); 60 4838 (1995) (α -amino ketones) CC 191 (1983) TL 31 1803 (1990) SL 788 (1993)

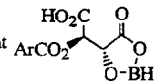
- $\text{H}_2\text{C}=\text{CHCH}_2\text{BR}_2$ (enantioselective) JOC 49 4089 (1984)
- $\text{R}_2\text{C}=\text{CRCHRB}(\text{Ipc})_2$ (enantioselective) JACS 105 2092 (1983); 107 2564 (1985); 108 293, 5919 (1986); 109 7553, 8120 (1987); 112 5875 (1990); 113 5337 (1991); 114 1090 (1992); 115 5302, 7152, 9842, 9925 (1993); 116 1753 (1994)
 TL 25 1215, 5111 (1984); 30 4763 (1989); 34 8439 (1993); 35 319, 985, 3405 (1994); 36 1189, 1581 (1995)
 JOC 51 432 (1986); 52 319, 3701 (1987); 54 1570 (1989); 55 1868 (1990); 56 401, 4875 (1991); 57 4793, 6608, 6614 (1992); 58 7768 (1993); 60 798, 2964, 5048 (1995)
 CC 877 (1987)
-  (enantioselective) JACS 111 1892 (1989); 112 7079 (1990)
-  (enantioselective) JOC 52 4831 (1987)
-  (enantioselective) JOC 52 4831 (1987)
-  (enantioselective) JOC 49 4089 (1984); 55 1868 (1990); 56 401 (1991); 57 6608, 6614 (1992)
 JACS 108 5919 (1986)
-  (enantioselective) JACS 112 2389 (1990)
 JOC 56 401 (1991); 57 6608, 6614 (1992)
- $\text{H}_2\text{C}=\text{CHC}(\text{=CH}_2)\text{CH}_2\text{B}(\text{Ipc})_2$ (enantioselective) TL 31 455 (1990)
- $\text{ROCH}=\text{CHCH}_2\text{BR}_2$ JACS 110 1535 (1988); 117 5958 (1995) (chiral); 114 3134 (1992) (chiral); 115 7612 (1993) (chiral)
 TL 31 6949 (1990) (chiral); 35 8973 (1994)
 JOC 57 1103 (1992) (chiral); 58 5587 (1993) (chiral)
- $\text{ClCH}=\text{CHCH}_2\text{BR}_2$ TL 36 4765 (1995) (chiral)
-  JOC 60 4686 (1995) (chiral)
- $\text{Me}_3\text{SiCR}=\text{CHCHRB}'_2$ JACS 112 4424 (1990)
 TL 32 3029 (1991)
- $\text{Me}_3\text{SiCH}=\text{CHCH}_2\text{Li}$, R_2BCl CC 1326 (1982)
- $\text{Me}_3\text{SiCH}_2\text{C}(\text{SiMe}_3)=\text{CHCH}_2\text{B}$  JOC 51 4733 (1986)

$R_2NSiMe_2CH=CHCH_2BR_2$	JOC 56 5243 (1991) (chiral)
$CH_3CH=CHCH(MMe_3)B \begin{array}{c} \diagup \\ \diagdown \end{array}$ (M = Si, Sn)	JACS 103 3229 (1981) CC 191 (1983)
$RCH=CHCH_2\bar{B}R_3$	CC 1072 (1980) JACS 103 1969 (1981)
$RCH=CHCH_2AlBr_2$	BSCF 1475 (1963)
$Me_3SiCH=CHCH_2Li, EtAlCl_2$	CC 1326 (1982)
$RCH=CHCH_2AlEt_2$	JACS 102 2118 (1980)
$ROCH=CHCH_2AlEt_2$	CC 845 (1982)
$H_2C=CHCH_2Al(i-Bu)_2, Sn(OTf)_2$, chiral diamine (enantioselective)	CL 97 (1986)
$CH_3CH=CHCH(OCON-i-Pr_2)Al(i-Bu)_2$	Angew Int 21 372 (1982)
$(RCH=CHCH_2AlR_3)Li$	JACS 108 4943 (1986); 113 5402 (1991) TL 31 4573 (1990) JOC 60 7778 (1995)
$(XCH=CHCH_2AlEt_3)Li$ (X = Me ₃ Si, PhSe)	TL 23 4597 (1982)
$(ROCH=CHCH_2AlEt_3)Li$	JOC 45 195 (1980) TL 23 4959 (1982)
$(RSCH=CHCH_2AlEt_3)Li$	JOC 45 195 (1980) TL 23 4959 (1982); 27 5947 (1986)
$(RCH=CHCH_2AlR_3)MgX$	TL 31 4573 (1990) JACS 113 5402 (1991) JOC 60 7778 (1995)
$H_2C=CHCH_2InCl_2$	JOC 58 5500 (1993)
$RCH=CHCHRSiX_3$ (diastereoselective)	"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 2.2, p 563 (review) Chem Rev 95 1293 (1995) (review)
$Me_2C=CHCH_2SiF_3, CsF$	TL 28 4081 (1987); 29 5667 (1988); 30 1099, 3419 (1989)
$R_2C=CHCH_2SiF_3, ROH, Et_3N$	JACS 112 257 (1990) (RCHO only)
$R_2C=CHCH_2SiX_3$ (X = F, OR), Et ₃ N	JACS 111 6429 (1989) (α -hydroxy ketones)
$R_2C=CHCH_2SiCl_3$	TL 34 3453 (1993) JOC 59 6620 (1994)
$RCH=CHCH_2SiCl_3$, chiral phosphoramidate (enantioselective)	JOC 59 6161 (1994)
$RCH=CHCH_2Si \begin{array}{c} \text{Ph} \\ \\ \text{---} \end{array}$	JOC 59 7152 (1994)

- $\text{RCH}=\text{CRCH}_2\text{SiMe}_3$, $\text{CF}_3\text{CO}_2\text{H}$ TL 30 6397 (1989) (intramolecular)
- $\text{RCH}=\text{CRCH}_2\text{SiMe}_3$, $\text{CF}_3\text{SO}_3\text{H}$ JOC 59 5130 (1994) (intramolecular)
- $\text{RCH}=\text{CRCHRSiMe}_3$, MgBr_2 JOC 58 999 (1993)
- $\text{RCH}=\text{CRCH}_2\text{SiMe}_3$, cat
 (enantioselective) SL 561 (1991)
 JACS 115 11490 (1993)
- $\text{RCH}=\text{CHCH}_2\text{SiMe}_3$, $\text{BF}_3 \cdot \text{OEt}_2$ TL 3513 (1978) (intramolecular); 26 823 (1985); 28 4959 (1987); 30 6397 (1989) (intramolecular); 31 3007, 7437 (1990) (both intramolecular); 32 2383 (1991); 33 5621, 5981 (1992); 36 8727 (1995)
 Helv 66 1655 (1983) (intramolecular)
 JOC 49 4214 (1984); 57 5247, 5403 (1992); 58 999 (1993); 59 3762, 5130 (intramolecular) (1994)
 CC 396 (1986)
 JACS 109 2512 (1987); 111 779 (intramolecular), 2967 (1989); 113 5378 (1991)
 SL 119 (1993)
- $\text{RCH}=\text{CHCHRSiMe}_3$, AlCl_3 JOMC 84 199 (1975)
 TL 2449 (1976); 429 (1979)
 Helv 66 1655 (1983) (intramolecular)
 SL 317 (1990)
 JOC 57 5403 (1992)
- $\text{H}_2\text{C}=\text{CRCH}_2\text{SiMe}_3$, EtAlCl_2 JACS 104 6879 (1982) (intramolecular)
 JOC 54 4278 (1989) (intramolecular)
- $\text{RCH}=\text{CRCH}_2\text{SiR}_3$, SiCl_4 JOC 59 5130 (1994) (intramolecular)
- $\text{RCH}=\text{CHCH}_2\text{SiMe}_3$, SnX_4 ($\text{X} = \text{Cl}, \text{Br}$) TL 3513 (1978) (intramolecular); 24 4765 (1983); 30 6397 (1989) (intramolecular); 31 1803, 3909 (1990); 32 1613, 5857 (1991); 36 6895 (1995)
 Helv 66 1655 (1983) (intramolecular)
 JOC 49 4214 (1984); 51 3290 (1986); 52 316 (1987); 57 5403 (1992); 58 999 (1993); 59 5130 (1994) (intramolecular)
 JACS 109 2512 (1987); 110 5768 (1988)
- $\text{RCH}=\text{CHCH}_2\text{SiMe}_3$, cat $\text{Cp}_2\text{Ti}(\text{OTf})_2$ TL 34 4309 (1993)
- $\text{RCH}=\text{CHCHRSiMe}_3$, TiCl_4 CC 927 (1976); 102 (1986)
 TL 1295 (1976); 1385 (1977); 2589 (1978); 429 (1979); 23 723 (1982); 24 2865, 5661 (1983); 26 823 (1985); 27 4485 (1986); 28 655 (intramolecular), 969 (chiral) (1987); 29 627 (1988) (intramolecular); 30 6067 (1989) (no rearrangement); 31 1803 (1990); 32 387, 1583, 2383 (1991); 34 1355 (1993); 36 1003, 6895, 8727, 8733 (1995)

$\text{RCH}=\text{CHCH}_2\text{SiMe}_3$, cat TiCl_4 , cat Cp_2TiCl_2
 $\text{RCH}=\text{CRCHRSiMe}_3$, ZnCl_2
 $\text{RCH}=\text{CHCH}_2\text{SiMe}_3$, various Lewis acid combinations
 $\text{H}_2\text{C}=\text{CBrCH}_2\text{SiMe}_3$, TiCl_4
 $\text{H}_2\text{C}=\text{C}(\text{OCONEt}_2)\text{CH}_2\text{SiMe}_3$; Me_3SiI , $\text{Me}_3\text{SiB}(\text{OTf})_4$ or $n\text{-Bu}_4\text{NF}$
 $\text{RCH}=\text{CHCHRSiMe}_3$, R_4NF
 $\text{RCH}=\text{CHCHRSiMe}_3$, $n\text{-Bu}_4\text{NF}\cdot\text{SiO}_2$
 $\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_2\text{CH}_2\text{NR}_2$; SnCl_4 , TiCl_4 , or $\text{BF}_3\cdot\text{OEt}_2$ (enantioselective)
 $\text{R}_2\text{C}=\text{CH}-\text{C}(\text{Me}_3)(\text{CH}_2\text{SiMe}_3)$, $n\text{-Bu}_4\text{NF}$
 $\text{Me}_3\text{SiCH}=\text{CHCH}_2\text{SiMe}_3$, $n\text{-Bu}_4\text{NF}$
 $\text{H}_2\text{C}=\text{CHC}(\text{CH}_3)=\text{CHCH}_2\text{SiMe}_3$, $n\text{-Bu}_4\text{NF}$
 $\left[\text{R}_2\text{C}=\text{CHCH}_2\text{Si} \left(\text{O} \begin{array}{c} \text{---} \text{O} \end{array} \begin{array}{c} \text{---} \text{O} \end{array} \begin{array}{c} \text{---} \text{O} \end{array} \right)_2 \right]^-$
 $\left[\text{R}_2\text{C}=\text{CHCH}_2\text{Si} \left(\text{O} \begin{array}{c} \text{---} \text{O} \end{array} \begin{array}{c} \text{---} \text{O} \end{array} \begin{array}{c} \text{---} \text{O} \end{array} \right)_2 \right]^-$
 $\text{RCH}=\text{CRCHRSnX}_3$

$\text{H}_2\text{C}=\text{CHCHRSnCl}_3$	JOC 58 5500 (1993) TL 34 1669, 3933 (1993) SL 87 (1994)
$\text{RCH}=\text{CHCH}_2\text{SnCl}_2\text{R}$	JOMC 197 45 (1980); 254 293 (1983); 258 291 (1983)
$\text{H}_2\text{C}=\text{CHCH}_2\text{SnCl}_2\text{R}$, HMPA	JOMC 258 291 (1983)
$(\text{R}_2\text{C}=\text{CHCH}_2)_2\text{SnBr}_2$ (R = H, Me)	JOMC 280 307 (1985)
$(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{SnBr}_2$, chiral diamine (enantioselective)	TL 36 6729 (1995)
$\text{H}_2\text{C}=\text{CHCH}_2\text{SnXR}_2$ (R = Br, OAc, NCS)	JOMC 258 291 (1983)
$\text{RCH}=\text{CHCHRSnClR}_2$	JOMC 162 37 (1978); 197 45 (1980); 226 149 (1982); 231 307 (1982)
$\text{H}_2\text{C}=\text{CHCH}_2\text{SnClR}_2$, HMPA	JOMC 258 291 (1983)
$(\text{H}_2\text{C}=\text{CHCH}_2)_4\text{Sn}$, CsF	JACS 110 7737 (1988)
$(\text{H}_2\text{C}=\text{CHCH}_2)_4\text{Sn}$, HCl, H_2O , THF	JACS 115 10356 (1993)
$(\text{H}_2\text{C}=\text{CHCH}_2)_4\text{Sn}$, cat $\text{Sc}(\text{OTf})_3$	JOC 58 6958 (1993)
$\text{RCH}=\text{CHCH}_2\text{SnR}'_3$, Δ (R' = Et, <i>n</i> -Bu)	TL 495 (1967); 28 5343 (1987); 34 957 (1993) (intramolecular) JOMC 35 C20 (1972) JACS 102 4548 (1980); 106 7970 (1984) (intramolecular); 112 8598 (1990); 117 6210 (1995) (intramolecular) Pure Appl Chem 53 2401 (1981) (review)
$\text{RCH}=\text{CHCH}_2\text{Sn}(\text{n-Bu})_3$, high pressure	JACS 112 8598 (1990) TL 33 3023 (1992)
$\text{RCH}=\text{CHCH}_2\text{Sn}(\text{n-Bu})_3$, $h\nu$ (no rearrangement)	TL 34 3457 (1993)
$\text{RCH}=\text{CRCHRSnR}_3$, <i>n</i> -Bu ₄ NF	TL 34 957 (1993) JOC 58 3557 (1993) (both intramolecular)
$\text{RCH}=\text{CHCHRSnR}_3$, <i>n</i> -Bu ₄ NF, TiCl_4	TL 34 1313 (1993) (intramolecular)
$\text{RCH}=\text{CRCHRSnR}_3$, Na-naphthalene	TL 34 957 (1993) JOC 58 3557 (1993) (both intramolecular)
$\text{RCH}=\text{CHCHRSnR}_3$, HOAc	TL 34 1313 (1993) (intramolecular)
$\text{RCH}=\text{CHCHRSnR}_3$, $\text{ClCH}_2\text{CO}_2\text{H}$	TL 34 1313 (1993) (intramolecular)
$\text{RCH}=\text{CHCH}_2\text{SnR}_3$, $\text{CF}_3\text{CO}_2\text{H}$	JACS 106 7970 (1984); 117 6210 (1995) TL 34 957, 1313 (1993) JOC 59 5133, 7889 (1994) (all intramolecular)

- $\text{RCH}=\text{CRCH}_2\text{SnR}_3$, $\text{Cl}_3\text{CCO}_2\text{H}$ TL 34 1313 (1993)
 JOC 59 5133 (1994)
 (both intramolecular)
- $\text{RCH}=\text{CRCH}_2\text{SnR}_3$, $\text{CF}_3\text{SO}_3\text{H}$ TL 34 957, 1313 (1993)
 JOC 59 5133 (1994)
 (all intramolecular)
- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, HBF_4 TL 34 957 (1993) (intramolecular)
- $\text{RCH}=\text{CHCHRSnR}_3$, HCl TL 34 1313 (1993) (intramolecular)
- $\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, LiClO_4 TL 33 1817 (1992)
 JOC 59 5128 (1994)
- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, MgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) TL 25 265, 1879, 1883, 3927 (1984); 28 4381
 (1987); 32 6939 (1991); 34 5487 (1993); 36 8557,
 8561 (1995)
 JOC 51 5478 (1986); 52 316 (1987); 54 6129 (1989);
 56 417 (1991); 58 1508 (1993); 59 3113, 5139,
 7889 (1994); 60 7870 (1995)
 JACS 109 7553 (1987); 113 5337 (1991); 117 6210
 (1995) (intramolecular)
 SL 283, 284 (1991); 81 (1993); 231 (1994)
- $\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, $\text{Mg}(\text{ClO}_4)_2$ TL 25 265 (1984)
- $\text{RCH}=\text{CRCHRSnR}_3$, $\text{BF}_3 \cdot \text{OEt}_2$ CL 919, 977 (1979); 1297, 1299 (1982)
 JACS 102 4548, 7107 (1980); 106 6835, 7970
 (intramolecular) (1984); 107 1778 (1985); 108
 4645 (1986); 110 984 (1988) (mechanism); 111
 7634 (1989); 112 4078, 5583, 8598 (1990); 114
 3910 (1992); 116 4674 (1994); 117 6210 (intra-
 molecular), 6619 (1995)
 CC 683 (1980)
 TL 23 4959 (1982); 25 265, 1879, 1883, 3927
 (1984); 26 6235 (1985); 27 5423 (1986); 28 139,
 2629, 3939, 5343 (1987); 29 3095 (1988); 31
 1803, 4573 (1990); 34 1313 (1993) (intramolec-
 ular)
 Tetr 40 2239 (1984)
 Organomet 4 1213 (1985) (chiral)
 JOC 51 863, 886, 1856, 2621, 5478 (1986); 52 316
 (1987); 55 3912 (1990); 57 5403 (1992); 59 5133
 (intramolecular), 5139, 7889 (1994); 60 5048
 (1995)
 SL 535 (1993)
- $\text{RCH}=\text{CRCH}_2\text{SnR}_3$, cat  (enantioselective) SL 653 (1992)
- $\text{RCH}=\text{CRCH}_2\text{SnR}_3$, AlCl_3 JACS 106 7970 (1984) (intramolecular)

- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, Et_2AlCl TL 25 1883 (1984); 34 957 (1993)
 (intramolecular)
 JACS 106 7970 (1984) (intramolecular)
- $\text{RCH}=\text{CRCH}_2\text{SnR}_3$, $(\text{Et}_2\text{Al})_2\text{SO}_4$ CL 977 (1979)
- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, InCl_3 JOC 60 1920 (1995)
- $\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, MeSiCl_3 or $\text{MeSi}(\text{OMe})_2\text{Cl}$ TL 33 1365 (1992)
- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, $t\text{-BuMe}_2\text{SiOTf}$ TL 34 4607 (1993) (intramolecular)
- Me_3SiOTf , Me_2S / $n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2$ /
 $n\text{-Bu}_4\text{NF}$ ($\text{RCHO} > \text{R}_2\text{CO}$) TL 36 3723 (1995)
- $\text{RCH}=\text{CRCH}_2\text{SnR}_3$, SnX_4 ($\text{X} = \text{Cl}, \text{Br}$) TL 25 1883, 3927 (1984); 26 6235 (1985); 28 2629
 (1987); 34 957 (1993) (intramolecular); 36 3353,
 6895 (1995)
 JACS 106 7970 (1984) (intramolecular); 110 984
 (1988) (mechanism); 111 8136 (1989) (mechan-
 ism); 112 5583 (1990)
 JOC 51 3290, 5478 (1986); 52 316 (1987); 58 165
 (no rearrangement), 3787 (1993); 59 5133 (1994)
 (intramolecular)
 SL 444, 585 (1992); 214 (1995) (all no
 rearrangement)
- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, SnBr_4 (no rearrangement) TL 34 3935 (1993); 36 3417 (1995)
- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, MeSnCl_3 TL 33 2369 (1992)
- $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, $n\text{-Bu}_2\text{SnCl}_2$
 (no rearrangement) JACS 114 5018 (1992)
- $\text{RCH}=\text{CRCH}_2\text{SnR}_3$, TiCl_4 TL 25 265, 1879, 1883, 3927 (1984); 28 2629
 (1987); 31 1803 (1990); 34 1313 (1993) (intra-
 molecular); 36 6895 (1995)
 JACS 106 7970 (1984) (intramolecular); 117 6210
 (1995) (intramolecular)
 CC 102 (1986)
 JOC 51 863, 1856, 3290, 5478 (1986); 54 4011
 (1989); 59 7889 (1994)
- $\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, $\text{TiCl}_4 \cdot \text{XPh}_3$
 ($\text{X} = \text{P}, \text{As}, \text{Sb}, \text{Bi}$) JOC 58 4783 (1993)
- $\text{H}_2\text{C}=\text{CRCH}_2\text{SnR}_3$, $i\text{-PrOTiCl}_3$ TL 36 3353 (1995)
- $\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, cat BINOL-TiCl_2
 (enantioselective) JACS 115 7001 (1993)
- $\text{H}_2\text{C}=\text{CRCH}_2\text{SnR}_3$, cat $\text{Ti}(\text{O-}i\text{-Pr})_4$, cat
 binaphthol (enantioselective) TL 34 7827 (1993)
 JOC 58 6543 (1993)
- $\text{H}_2\text{C}=\text{CRCH}_2\text{SnR}_3$, cat $\text{Ti}(\text{O-}i\text{-Pr})_4$, cat
 binaphthol, molecular sieves, $(\text{CF}_3\text{SO}_3\text{H})$
 (enantioselective) JACS 115 8467 (1993)
 JOC 58 6543 (1993)
- $\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, cat $\text{BINOL-Zr}(\text{O-}i\text{-Pr})_2$
 (enantioselective) TL 36 7897 (1995)

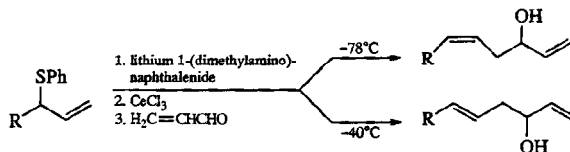
$\text{RCH}=\text{CHCH}_2\text{SnR}_3$, ZrCl_4	TL 25 1883 (1984) JACS 106 7970 (1984) (intramolecular)
$\text{RCH}=\text{CRCH}_2\text{SnR}_3$, FeCl_3	JACS 106 7970 (1984) (intramolecular)
$\text{RCH}=\text{CHCH}_2\text{SnR}_3$, CoCl_2 (no rearrangement)	TL 30 2421 (1989)
$\text{RCH}=\text{CHCH}_2\text{SnR}_3$, ZnX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)	TL 495 (1967); 25 265, 1879, 1883, 3927 (1984) JOC 54 4011 (1989); 55 6071 (1990); 59 3055 (1994)
$\text{RCH}=\text{CHCH}_2\text{SnR}_3$, SnI_2	TL 34 957 (1993) (intramolecular)
$\text{H}_2\text{C}=\text{CHCH}_2\text{SnR}_3$, cat $\text{Yb}(\text{OTf})_3$	TL 35 4639 (1994)
$\text{ROCHRCH}=\text{CHCH}_2\text{Sn}(\text{n-Bu})_3$, Δ	TL 29 2479 (1988)
$\text{ROCHRCH}=\text{CHCH}_2\text{SnR}_3$, SnCl_4 (no rearrangement)	TL 30 6239 (1990)
$\text{ROCHRCH}=\text{CHCH}_2\text{SnR}_3$, SnCl_4	TL 33 1369 (1992)
$\text{RCH}=\text{CHCH}(\text{OR})\text{SnR}_3$, Δ	CC 1115 (1982); 800 (1984) TL 28 527 (1987)
$\text{RCH}=\text{CHCH}(\text{OR})\text{SnR}_3$, $\text{BF}_3 \cdot \text{OEt}_2$	TL 28 527 (1987) (intramolecular); 29 1657, 3899, 4811 (1988) (all intramolecular); 32 13, 453, 2101 (1991) JOC 53 1616 (1988) (intramolecular); 56 5493 (1991)
$\text{RCH}=\text{CHCH}(\text{OR})\text{SnR}_3$, $\text{BF}_3 \cdot \text{OEt}_2$ (no rearrangement)	TL 30 309 (1989) (intramolecular)
$\text{RCH}=\text{CHCH}(\text{OR})\text{SnR}_3$, InCl_3	JOC 60 1920 (1995)
$\text{ROCH}=\text{CHCHRSnR}_3$, MgBr_2	TL 28 139 (1987); 33 6077 (1992) JOC 54 896 (1989); 56 483 (1991) (chiral); 57 1958 (1992); 59 3413, 5139, 7825 (1994) JACS 114 9434 (1992); 116 8536 (1994) (chiral) SL 1007 (1992)
$\text{ROCH}=\text{CHCHRSnR}_3$, $\text{BF}_3 \cdot \text{OEt}_2$	TL 28 143 (1987); 30 2183 (1989); 32 2101, 4505 (intramolecular), 7069 (intramolecular) (1991); 36 5777 (1995) (intramolecular) JOC 56 483 (1991) (chiral); 57 7003 (1992) (chiral); 58 5876, 6229 (1993) (both chiral); 59 2848 (intramolecular), 3413, 4122, 5139, 6614, 7825, 7833 (1994); 60 2662 (1995) JACS 113 647 (1991); 116 8536 (1994) (chiral) SL 537 (1992); 1252 (1995) (intramolecular)
$\text{ROCH}=\text{CHCH}_2\text{SnR}_3$, AlCl_3	JOC 57 7003 (1992) (chiral)
$\text{ROCH}=\text{CHCHRSnR}_3$, InCl_3	JOC 60 1920 (1995)
$\text{ROCH}=\text{CHCH}_2\text{SnR}_3$, SnCl_4	JOC 57 7003 (1992) (chiral)
$\text{ROCH}=\text{CHCHRSnR}_3$, TiCl_4	TL 30 7037 (1989) JOC 57 7003 (1992) (chiral)

$R_3SiOCH=CHCHRSnR_3$, $BF_3 \cdot OEt_2$	JOC 57 7158 (1992)
$(H_2C=CHCH_2)_2SnR_2$, $BF_3 \cdot OEt_2$	CL 1529 (1983) (chiral R) Organomet 4 1213 (1985)
$H_2C=CHC(=CH_2)CH_2SnMe_3$, $BF_3 \cdot OEt_2$	CL 977 (1979)
$R_2C=CRCH_2Sn \left[\begin{array}{c} O-CHCO_2Et \\ O-CHCO_2Et \end{array} \right]^-$ (enantioselective)	JOC 52 5447 (1987)
$CH_3CH=CHCH_2Sb(n-Bu)_4$, $AlCl_3$	JOC 57 774 (1992)
$Me_3SiCH=CHCH_2Sb(n-Bu)_4$ (no rearrangement)	TL 34 1621 (1993)
$RCH=CHCH_2TiCp \left[\begin{array}{c} OPh_2CHO \\ \\ OPh_2CHO \end{array} \right] CMe_2$ (enantioselective)	JACS 114 2321 (1992)
$RCH=CHCH_2TiCp_2$	TL 23 4589 (1982) JOMC 224 327 (1982) CC 921 (1983)
$RCH=CHCH_2Ti(\text{substituted } Cp)_2$ (enantioselective)	JOC 54 4154 (1989)
$RCH=CHCH_2TiCp_2X$ ($X = Cl, Br, I$)	CC 342, 1140 (1981); 98 (1986) TL 22 243 (1981) JOC 54 6129 (1989)
$RCH=CHCH_2Ti(OR)_3$	Angew Int 19 1011 (1980); 21 135 (1982) Helv 65 1085, 1972 (1982) JACS 104 7663 (1982); 107 1691 (1985); 113 1866 (1991) Ber 118 1441 (1985) Tetr 42 2803 (1986) TL 28 869 (1987) JOC 54 6129 (1989)
$RSCH=CHCH_2Ti(O-i-Pr)_3$	JACS 104 7663 (1982) BCSJ 57 2781 (1984) JOC 57 3078 (1992)
$(i-PrO)_3TiOCH_2CH=CHCH_2Ti(O-i-Pr)_3$	JOC 55 1528 (1990)
$RCH=CHCH_2Ti(NEt_2)_3$	Ber 118 1441 (1985)
$CH_3CH=CHCH(OCN-i-Pr)_2Ti(NEt_2)_3$	Angew Int 21 372 (1982)
$[Me_3SiCH=CHCH_2Ti(O-i-Pr)_4]Li$	Ber 118 1441 (1985)
$[H_2C=CHCH_2Ti(O-i-Pr)_4]MgCl$	TL 23 5259 (1982) ($RCHO > R_2CO$) Ber 118 1441 (1985) JOC 58 2686 (1993)
$[H_2C=CHCH_2Ti(NMe_2)_4]Li$	TL 23 5259 (1982) ($R_2CO > RCHO$)
$RCH=CHCH_2ZrCp_2Cl$	TL 22 2895 (1981) JOC 54 6129 (1989) SL 359 (1994)

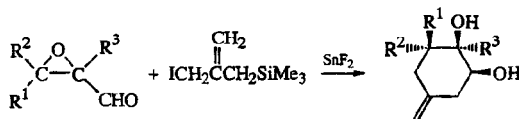
$\text{RCH}=\text{CHCH}_2\text{ZrCp}_2\text{OR}$	TL 33 1295 (1992)
$\text{ROCH}=\text{CHCR}_2\text{ZrCp}_2\text{OR}$	TL 33 7873 (1992) (with and without rearrangement)
$\text{R}_3\text{SiOCH}_2\text{CH}=\text{CHCH}_2\text{ZrCp}_2\text{OSiR}_3$	TL 36 7137 (1995)
$(\text{H}_2\text{C}=\text{CHCH}_2)_4\text{Zr}$	JACS 105 4833 (1983)
$\text{H}_2\text{C}=\text{CHCH}_2\text{CrCl}_2$	TL 27 5351 (1986) (β -hydroxy ketone)
$\text{RCH}=\text{CHCH}_2\text{CrCl}_2$	JOC 54 6129 (1989)
$\text{—} \left\langle \text{—MoCl(NO)CpR} \right\rangle$ (enantioselective)	JACS 111 1937 (1989) TL 30 1769 (1989)
$(\eta^3\text{-crotyl})\text{MoX(NO)Cp}$ ($\text{X}=\text{Cl, Br, I, OTs}$) (enantioselective)	TL 32 1271 (1991)
$\text{H}_2\text{C}=\text{CHCH}_2\text{Fe(CO)}_2\text{Cp, BF}_3\cdot\text{OEt}_2/\text{NaI}$	TL 32 3001, 4639 (1991)
$\text{CuCN}\cdot\text{LiCl}/\text{Li-naphthalene}/\text{allylic chloride}$ or acetate	JACS 114 5110 (1992)
$\text{ThCu(CN)Li}/\text{Li-naphthalene}/\text{allylic chloride}$	JOC 58 2492 (1993)
$\text{H}_2\text{C}=\text{CHCH}_2\text{Cu}\cdot\text{SMe}_2/\text{MgBr}_2$	TL 28 869 (1987)
$(\text{Me}_3\text{SiC}\equiv\text{CCH}=\text{CHCH}_2)_2\text{CuLi}$ (no rearrangement)	JACS 115 10400 (1993)
$\text{RCH}=\text{CRCH}_2\text{Cu}\cdot\text{ZnI}_2$	JACS 112 6146 (1990) JOC 58 2694 (1993)
$\text{H}_2\text{C}=\text{CRC(=CH}_2\text{)CH}_2\text{Cu(CN)ZnI}$	JOC 58 2694 (1993)
$\text{H}_2\text{C}=\text{CRC(=CH}_2\text{)CH}_2\text{CH}_2\text{Cu(CN)ZnI}$	TL 32 1855 (1991) JOC 58 2694 (1993)
$\text{RCH}=\text{CHCHRZnX}$	BSCF 1475 (1963) TL 3829 (1975) (with and without rearrangement); 31 4573 (1990) JOC 54 5198 (1989); 57 5425 (1992); 60 7778 (1995)
$\text{H}_2\text{C}=\text{C(SiMe}_3\text{)CH}_2\text{ZnCl}$	SL 277 (1993)
$\text{H}_2\text{C}=\text{C(SiMe}_3\text{)CH}_2\text{ZnCl, BF}_3\cdot\text{OEt}_2$	SL 279 (1993)
$\text{ClCH}=\text{CHCH}_2\text{ZnCl}$	TL 34 3145 (1993)
$(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{Zn}$	BSCF 974 (1962); 4038 (1969) Pure Appl Chem 53 1163 (1981) JOC 51 3742 (1986); 52 1141 (1987); 58 2232 (1993); 60 7778 (1995) TL 28 869 (1987)
$\text{H}_2\text{C}=\text{CHC(=CH}_2\text{)CH}_2\text{ZnBr}$	Syn 742 (1979)
$(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{Cd}$	BSCF 4038 (1969)
$\text{RCH}=\text{CHCH}_2\text{CeCl}_2$ (no rearrangement)	JACS 113 1866, 2313 (1991); 114 5018 (1992) TL 35 8453 (1994)

$\text{RCH}=\text{CHCH}_2\text{SmCp}_2$

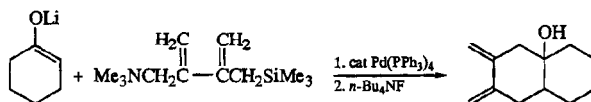
TL 32 629 (1991)

 $\text{Cl}_2\text{CeOCH}_2\text{CH}=\text{CHCH}_2\text{CeCl}_2$ (no rearrangement) JOC 55 1528 (1990)


JACS 109 4710 (1987)



JACS 109 576 (1987)



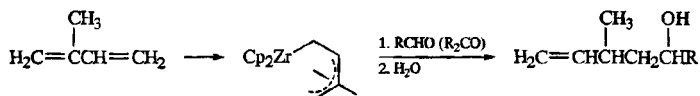
CC 570 (1987)


 PrMgBr , $\text{Cp}_2\text{TiCl}_2/\text{R}_2\text{CO}$ or RCHO
TL 21 365 (1980); 36 5595 (1995) (chiral)
CC 342 (1981)
 LiH , ZnI_2 , cat $\text{Cp}_2\text{TiCl}_2/\text{R}_2\text{CO}$ or RCHO

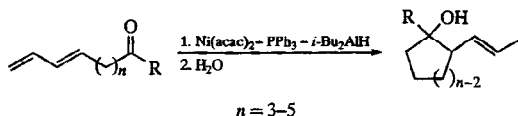
JOC 59 5521 (1994)

 Cl_3SiH , cat $\text{Pd}(\text{PPh}_3)_4/\text{RCHO}$, DMF

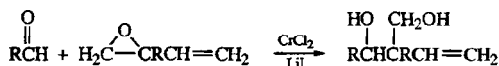
JOC 59 6620 (1994)



CL 671 (1981)



JACS 116 9771 (1994)



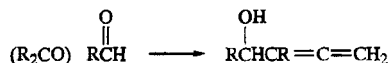
JOC 55 1705 (1990)


 $\frac{\text{M}}{\text{B(OR)}_2}$
 $\text{SiMe}_3 \text{ (TiCl}_4\text{)}$

TL 36 2441 (1995)

JOC 60 486 (1995)

TL 32 4509, 4513 (1991)



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 1.3, p 81

 $\text{RC}\equiv\text{CCH}_2\text{Br, SnCl}_2, \text{NaI}$

CL 621 (1981)

JOC 60 796 (1995)

 $\text{RC}\equiv\text{CCH}_2\text{Br, Ti(O-}i\text{-Pr)}_4, i\text{-PrMgBr}$

TL 36 3207 (1995)

 $\text{H}_2\text{C}=\text{C}=\text{C(OR)Li}$

Rec Trav Chim 87 1179 (1968)

SL 179 (1991); 105 (1993) (chiral)

JOC 59 67 (1994)

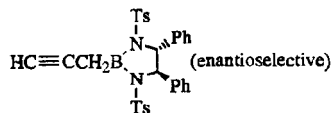
 $\text{RC}\equiv\text{CCH}_2\text{MgX}$

JOC 54 5198 (1989)

 $\text{Me}_3\text{SiC}\equiv\text{CCH}_2\text{BR}_2$

TL 30 1311 (1989)

JOC 60 8130 (1995) (chiral)



JACS 112 878 (1990)

TL 35 8545 (1994)

 $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{InCl}_2$

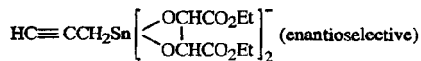
JOC 58 5500 (1993)

 $\text{H}_2\text{C}=\text{C}=\text{CRSiCl}_3$

JACS 117 6392 (1995)

 $\text{RC}\equiv\text{CCH}_2\text{SiMe}_3, \text{Lewis acid}$

TL 36 5499 (1995) (intramolecular)



JOC 52 5447 (1987)

 $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{SnCl}_3$

JOC 58 5500 (1993)

 $n\text{-Bu}_3\text{SnCR}=\text{C}=\text{CHR}, n\text{-BuSnCl}_3$

JOC 60 5550 (1995)

 $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{Sb}(n\text{-Bu})_4$

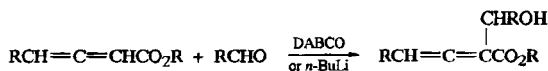
TL 32 6579 (1991)

 $\text{RC}\equiv\text{CCH}_2\text{ZnX}$

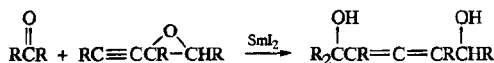
JOC 54 5198 (1989)

 $\text{RC}\equiv\text{CCH}_2\text{SmCp}^*_2$

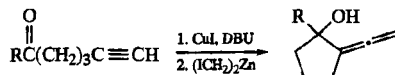
TL 36 6283 (1995)



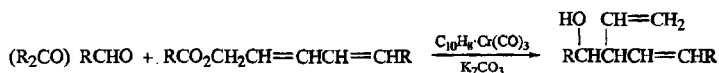
JOC 58 5952 (1993)



TL 36 2501 (1995)



JOC 58 2694 (1993)



JOC 59 712 (1994)

M

Be

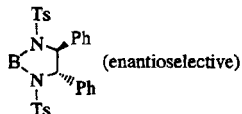
BCSJ 53 1101 (1980)

Mg

BCSJ 53 1089 (1980)

B(OMe)₂

Helv 65 1258 (1982)



JACS 117 9608 (1995)

SnR₃ (BF₃·OEt₂)

CL 1299 (1982)

SnR₃ (TiCl₄)

JCS Perkin I 2581 (1992)

Zn

BCSJ 53 1101 (1980)

MLewis acidSiR₃BF₃·OEt₂

TL 21 3783 (1980)

JCS Perkin I 2581 (1992)

TiCl₄

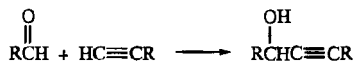
JOC 45 1721 (1980)

Organomet 1 1651 (1982)

JACS 106 3240 (1984)

TL 28 5921 (1987)

SnR_3	$\text{BF}_3 \cdot \text{OEt}_2$	CL 1299 (1982); 1683 (1983) JCS Perkin I 2581 (1992)
	AlCl_3	CL 1683 (1983)
	TiCl_4	JOC 47 1789 (1982)
	ZnCl_2	SL 731 (1994)

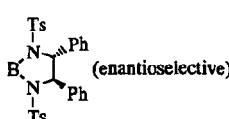



$\text{GaI}_3, n\text{-Bu}_3\text{N}$	TL 36 7277 (1995)
$\text{Sn}(\text{OTf})_2, \text{amine}$	JOC 56 4091 (1991)
$\text{Sn}(\text{OTf})_2, \text{SnCl}_2, \text{amine}$	JOC 56 4091 (1991)
$\text{SnCl}_4, n\text{-Bu}_3\text{N}$	CL 2479 (1992)



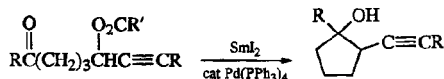
Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 1.3, p 81

M

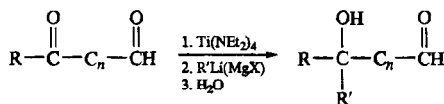
Li	JOC 47 2225 (1982); 53 286 (1988) JACS 114 644 (1992) SL 745 (1995)
MgX	JACS 90 6141 (1968); 109 8051 (1987); 114 9836 (1992) Compt Rend C 269 342 (1969) TL 37 (1972); 27 3311 (1986); 29 2819 (1988) BSCF 3371 (1973) JOC 47 2225 (1982); 54 5198 (1989); 58 3912 (1993)
$\text{B}(\text{OR})_2$	JOMC 92 17 (1975); 195 137 (1980) JACS 104 7667 (1982); 108 483 (1986) (both chiral) TL 27 1175 (1986); 30 3789 (1989); 33 2327 (1992) JOC 51 886 (1986); 60 1170 (1995) (chiral)
	JACS 112 878 (1990)
BEt_2	JACS 106 3875 (1984)
	JOC 50 1577 (1985) ($\text{RCHO} > \text{R}_2\text{CO}$); 60 544 (1995) TL 34 15 (1993)
$\text{Al}_{2/3}\text{Br}$	Ann 682 62 (1965) TL 37 (1972) BSCF 3371 (1973)
SiCl_3	JACS 117 6392 (1995)

M

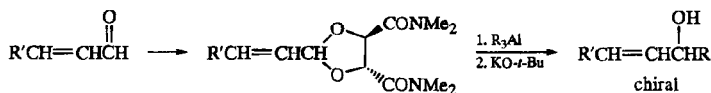
SiMe ₃ , (TiCl ₄)	JOC 45 3925 (1980); 51 3870 (1986) TL 34 2383, 2387 (1993)
R ₃ Sn (RLi)	JOC 55 441 (1990)
<i>n</i> -Bu ₃ Sn (MgBr ₂)	JOC 56 3211 (1991); 57 1242 (1992); 60 5556 (1995)
<i>n</i> -Bu ₃ Sn (BF ₃ ·OEt ₂)	JOC 55 6246 (1990); 56 3211, 6264 (intramolecular) (1991); 57 1242, 3387 (1992); 59 3509 (1994); 60 5556, 7230 (1995)
<i>n</i> -Bu ₃ Sn (SnCl ₄)	JOC 59 3509 (1994); 60 5556 (1995)
<i>n</i> -Bu ₃ Sn [Ti(O- <i>i</i> -Pr) ₄ , BINOL; enantioselective]	TL 35 8323 (1994)
<i>n</i> -Bu ₄ Sb	TL 32 6579 (1991); 34 1621 (1993)
Ti(OR) ₃	JOC 47 2225 (1982); 51 886 (1986)
TiX(O- <i>i</i> -Pr) ₂ (X = Cl, Br, OAc, OCO ₂ Et)	TL 36 3207 (1995)
ZrCp ₂ OR (BF ₃ ·OEt ₂)	TL 33 3769 (1992)
Cu	JACS 109 5437 (1987)
Cu(CN)ZnI	TL 32 1855 (1991) JOC 58 2694 (1993)
ZnX	BSCF 3371 (1973); 1248 (1975) TL 22 1579 (1981); 32 3131 (1991); 33 3117 (1992) JOC 47 2225 (1982); 54 5198 (1989); 58 6166 (1993) SL 493 (1995)
SmCp* ₂	TL 36 6283 (1995)



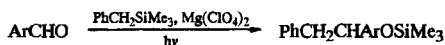
JOC 59 702 (1994)



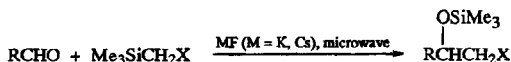
CC 406 (1983)



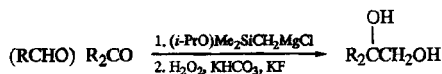
JACS 106 5004 (1984)



JACS 116 5503 (1994)

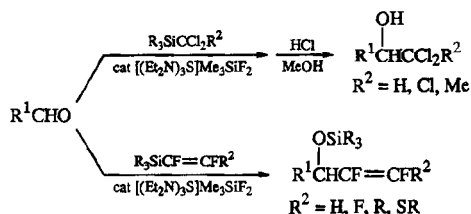

 $\text{X} = \text{CO}_2\text{R}, \text{CN}$

TL 32 1179 (1991)

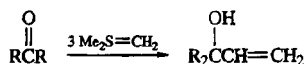


TL 25 4245 (1984); 27 4885 (1986)

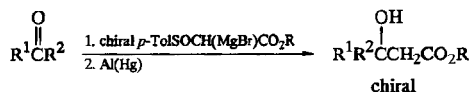
Org Syn Coll Vol 8 315 (1993)



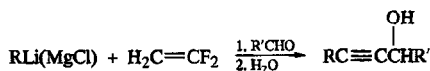
JACS 107 4085 (1985)



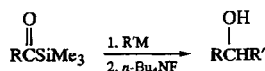
TL 35 2009 (1994)



CC 162 (1977)

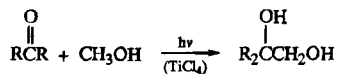

 $\text{R} = 1^\circ, 2^\circ, 3^\circ \text{ alkyl; allyl; vinyl}$

TL 23 4325 (1982)

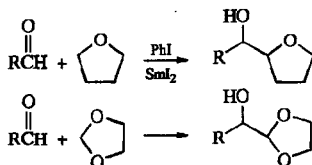
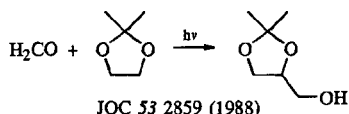

 $\text{R}'\text{M} = \text{RLi}, \text{RMgX}, \text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$

JACS 110 4826 (1988) (diastereoselective)

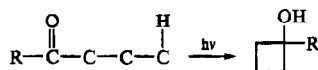
2.2. Miscellaneous Additions



IOC 45 3778 (1980); 53 5567 (1988)



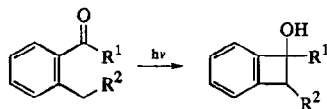
TL 28 5877 (1987)



JCS Perkin II 7, 14 (1976)

JACS 108 3841 (1986); 109 3017 (1987); 114 3870 (1992)

IOC 52 5521 (1987)

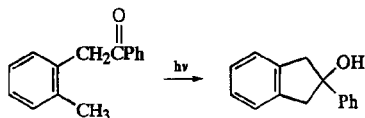


Tetr 32 405 (1976) (review)

TL 29 3087 (1988); 32 263 (1991)

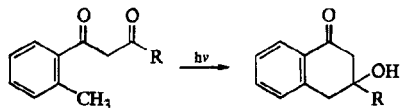
JACS 113 709 (1991)

IOC 57 2922, 6222 (1992)

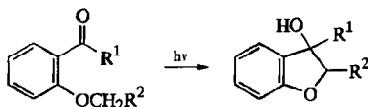


JACS 105 4484 (1983); 113 9630, 9640 (1991)

TL 30 5389 (1989); 32 165 (1991)



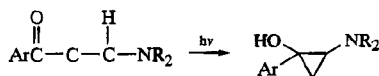
IOC 53 5597 (1988)



JACS 112 5199 (1990); 115 7914 (1993)

TL 31 1819, 3775 (1990); 32 895 (1991)

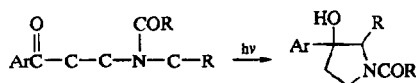
JOC 60 1303 (1995)



Arch Pharm 303 725 (1970); 307 584 (1974); 311 341 (1978)

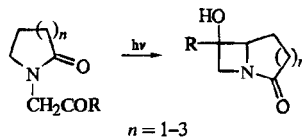
J Prakt Chem 327 51 (1985)

TL 32 7151 (1991); 34 6737 (1993)



J Prakt Chem 327 51 (1985)

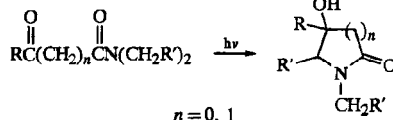
Monatsh 120 253 (1989)



$n = 1-3$

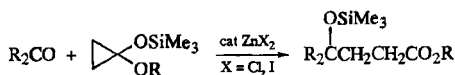
Tetr 46 7751 (1990)

JOC 58 3783 (1993)



$n = 0, 1$

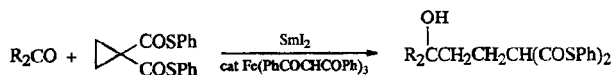
See page 1861, Section 8.



JOC 50 2802 (1985)

JACS 109 8056 (1987)

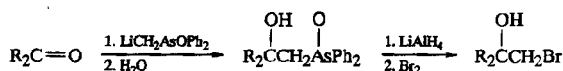
TL 28 337 (1987)



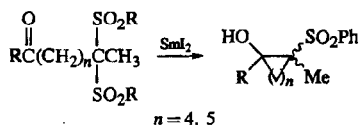
TL 35 7805 (1994)

		$\text{R}'\text{CHO} \longrightarrow \begin{array}{c} \text{OH} \\ \\ \text{RCHR}' \end{array}$
<u>R</u>	<u>Reagents</u>	
CHX_2 (X = Cl, Br, I)	H_2CX_2 , LiNR_2	JACS 96 3010 (1974) BCSJ 50 1588 (1977)
CF_3	HCF_3 , $\text{R}_4\text{N} \left(\text{N} \begin{array}{c} \text{O} \\ \\ \text{C} \end{array} \text{C}_4\text{H}_7 \right)$	JOC 56 2 (1991)
CCl_3	HCCl_3 , KOH	JACS 70 1189 (1948); 72 5012 (1950) JOC 50 2527 (1985); 52 944 (1987)
	HCCl_3 , NaOH, $(\text{PhCH}_2\text{NEt}_3)\text{Cl}$	Ber 110 96 (1977)
	HCCl_3 , KO- <i>t</i> -Bu	Ber 91 2664 (1958) JOC 50 2527 (1985)
	HCCl_3 , NaNH_2	Ber 96 420 (1963)
	HCCl_3 , LiNR_2	JACS 96 3010 (1974) BCSJ 50 1588 (1977)
	HCCl_3 , NaH	JOC 50 2527 (1985)
	$\text{N} \begin{array}{c} \text{O} \\ \\ \text{C} \end{array} \text{Cl}_3$, $\text{Cl}_3\text{CCO}_2\text{H}$	TL 33 3435 (1992)
	$(\text{CH}_3)_2\text{SiMe}_3$, K_2CO_3 , crown-6 (TMS ether)	TL 26 1175 (1985); 32 1031 (1991) JOC 57 3731 (1992)
	$\text{Cl}_3\text{CCO}_2\text{SiMe}_3$, KF or $[(\text{Me}_2\text{N})_3\text{S}]\text{Me}_3\text{SiF}_2$	Syn Commun 17 1047 (1987)
CBr_3	HCBBr_3 , KO- <i>t</i> -Bu	Ber 91 2664 (1958)
	HCBBr_3 , NaNH_2	Ber 96 420 (1963)
	HCBBr_3 , LiNR_2	JACS 96 3010 (1974) BCSJ 50 1588 (1977)
	$\text{NaO}_2\text{CCBr}_3$, $\text{Br}_3\text{CCO}_2\text{H}$	TL 33 3435 (1992)
CCl_2CF_3	$\text{CF}_3\text{CCl}_2\text{H}$, $n\text{-Bu}_4\text{N} \left(\text{N} \begin{array}{c} \text{O} \\ \\ \text{C} \end{array} \text{C}_4\text{H}_7 \right)$	JOC 56 2 (1991)
		$\text{R}'\text{CHO} + \text{RX} \xrightarrow{\text{electrolysis}} \begin{array}{c} \text{OH} \\ \\ \text{RCHR}' \end{array}$
<u>R</u>	<u>RX</u>	
CF_3	CF_3Br	TL 27 3129 (1986); 32 6567 (1991)
$n\text{-C}_4\text{F}_9$	$n\text{-C}_4\text{F}_9\text{I}$	TL 32 6567 (1991)
$\text{CF}_2\text{CO}_2\text{Me}$	$\text{ClCF}_2\text{CO}_2\text{Me}$	TL 32 6567 (1991)
CCl_2CF_3	CCl_3CF_3	TL 32 6567 (1991)
CCl_3	CCl_4	TL 1521 (1978); 27 3129 (1986)
	CCl_4 , HCCl_3	TL 22 871 (1981) JACS 106 259 (1984) JOC 50 2527 (1985)

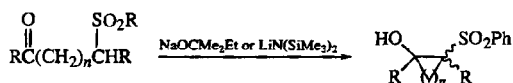
$\text{CCl}_2\text{CO}_2\text{Me}$	$\text{Cl}_3\text{CCO}_2\text{Me}$, $\text{HCCl}_2\text{CO}_2\text{Me}$	JACS 106 259 (1984) JOC 50 2527 (1985); 53 1364 (1988)
CHClCO_2Me	$\text{Cl}_2\text{CHCO}_2\text{Me}$	TL 27 3129 (1986)
CHMeCO_2Et	$\text{ClCHMeCO}_2\text{Et}$	TL 27 3129 (1986)
CHPhCO_2Me	$\text{BrCHPhCO}_2\text{Me}$, $\text{PhCH}_2\text{CO}_2\text{Me}$	JOC 50 2527 (1985)
$\text{CH}(\text{CO}_2\text{Me})_2$	$\text{BrCH}(\text{CO}_2\text{Me})_2$, $\text{H}_2\text{C}(\text{CO}_2\text{Me})_2$	JOC 50 2527 (1985)
allylic	allylic chloride	TL 22 1895 (1981); 27 3129 (1986)
	allylic chloride or bromide	JOC 54 5608 (1989)
CH_2Ph	PhCH_2Cl	TL 27 3129 (1986)
Ar	ArCl	TL 27 3129 (1986)



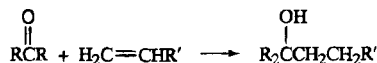
Ber 115 645 (1982)



JACS 114 5432 (1992)


 JOC 51 4735 (1986) ($n = 11$)

 TL 29 6951 (1988) ($n = 11$); 32 4925 (1991) ($n = 11$); 34 7895 (1993) ($n = 9$); 36 35 (1995) ($n = 9$)

 SL 249 (1995) ($n = 13$)


electrolysis

JACS 93 5284 (1971); 100 545 (1978); 110 3622

(1988); 111 1211 (1989) (all intramolecular)

 JOC 50 2202 (1985) (intramolecular, $\text{R}' = \text{CO}_2\text{Et}$);

51 1041 (1986) (intramolecular); 53 2287 (1988)

 (intramolecular; $\text{R}' = \text{CO}_2\text{R}$, CN); 54 6001 (1989);

 59 5017 (1994) (intramolecular, $\text{R}' = \text{CO}_2\text{R}$)

TL 31 487 (1990) (intramolecular); 36 5041 (1995)

(inter- and intramolecular)

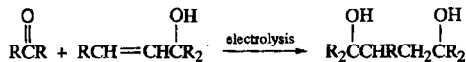
 hv, Et_3N

TL 26 4591 (1985); 28 4545 (1987); 29 6113 (1988)

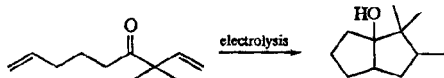
(all intramolecular)

JOC 58 2351 (1993)

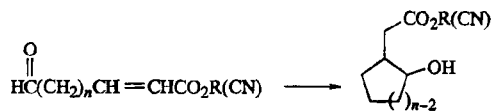
hv, Et ₃ N, HMPA	TL 30 7361 (1989) (intramolecular)
hv, HMPA	TL 26 4591 (1985) (intramolecular) JOC 51 4196 (1986) (intramolecular)
Li, THF	JOC 46 2622 (1981)
Li, NH ₃ , <i>t</i> -BuOH	IACS 110 5064 (1988)
Na, moist ether	CC 206 (1965) (intramolecular)
Na, THF	JOC 46 2622 (1981)
Na, <i>t</i> -BuOH	JOC 44 2369 (1979)
Mg, cat HgCl ₂	JOC 59 1428 (1994) (intramolecular; R' = CO ₂ R, CN, SPh)
Mg, Me ₃ SiCl	JOC 50 5193 (1985) (intramolecular)
[V ₂ Cl ₃ (THF) ₆] ₂ [Zn ₂ Cl ₆]	JOC 56 4983 (1991) (intramolecular, R' = CO ₂ R)
Zn, Me ₃ SiCl, lutidine	TL 24 2821 (1983) (intramolecular)
SmI ₂	TL 28 4367 (1987) (intramolecular); 30 1063 (intramolecular), 2837 (1989); 33 1517 (1992) (intramolecular); 36 1633 (1995) (intramolecular) IACS 110 5064 (1988); 111 6463, 8236 (1989) (both intramolecular); 112 5601 (1990) (intramolecular) JOC 54 5841 (1989) (intramolecular, R' = CO ₂ R); 57 3132, 6357 (intramolecular) (1992); 58 6303 (1993) (intramolecular); 59 3186, 5532 (1994) (both intramolecular); 60 872 (1995) (intramolecular) SL 158 (1993) (intramolecular); 729 (1995)
Ph ₂ SiH ₂ , cat Cp ₂ Ti(PMe ₃) ₂ , cat PMe ₃	JACS 117 6785 (1995) (intramolecular)
(EtO) ₂ SiH, cat Cp ₂ Ti(PMe ₃) ₂	JACS 117 6787 (1995) (intramolecular)
<i>n</i> -Bu ₃ SnH	JACS 108 5893 (1986) TL 29 75 (1988); 30 4939 (1989); 33 1835 (1992) (polycyclics); 35 129 (1994) (R' = CO ₂ R); 36 417 (1995) JOC 58 6303 (1993) (all intramolecular)



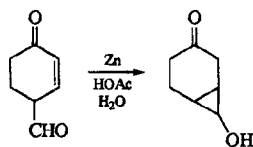
JOC 59 273 (1994)



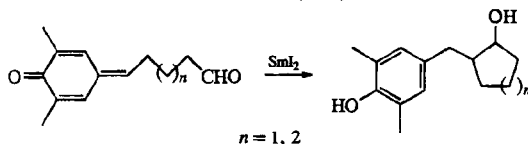
JOC 54 4022 (1989)



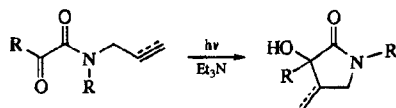
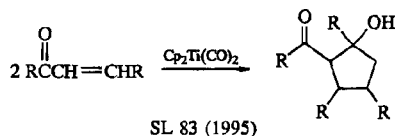
See page 1809, Section 6. For the analogous formation of lactones, see page 1861, Section 8.



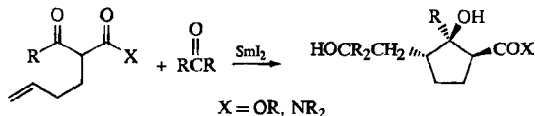
TL 35 5755 (1994)



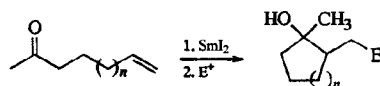
JOC 57 6883 (1992)



TL 35 1541 (1994)

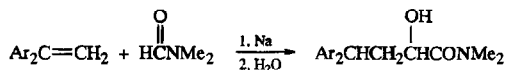


JOC 56 1439 (1991)



$n = 1, 2$; $\text{E}^+ = \text{RCHO}, \text{R}_2\text{CO}, \text{Ac}_2\text{O}, \text{O}_2, (\text{PhS})_2, (\text{PhSe})_2, (\text{H}_2\text{C}=\text{NMe}_2)\text{I}, \text{CO}_2$

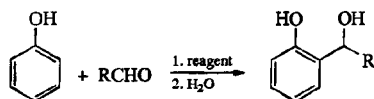
JOC 57 3132 (1992); 60 872 (1995)



TL 33 5601 (1992)



JACS 108 4676 (1986); 110 3622 (1988)
JOC 59 1407 (1994)



Reagent

base?

TL 30 1121 (1989)

LiOH or NaOH

JOC 58 4023 (1993)

EtMgBr

CC 794 (1987)

JOC 53 4919 (1988)

PhBCl₂, Et₃N

TL 34 5527 (1993)

chiral RO(Et)AlCl

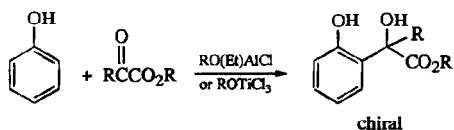
JOC 50 5018 (1985)

Ti(O-*i*-Pr)₄

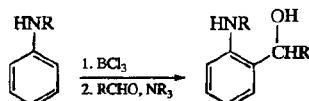
CC 794 (1987)

JOC 53 4919 (1988)

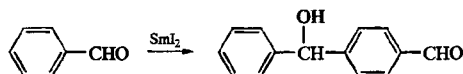
TL 36 1125 (1995) (intramolecular)



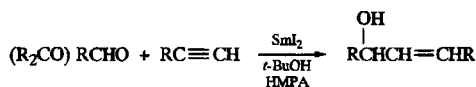
JOC 53 1779 (1988)



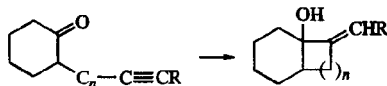
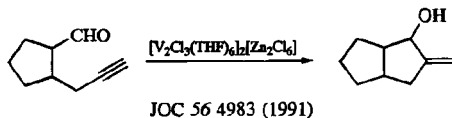
JACS 100 4842 (1978)



TL 34 335 (1993)



TL 32 4921 (1991)



electrolysis

CL 1233 (1976)

JACS 110 3622 (1988)

hv, HMPA

JOC 51 4196 (1986)

TL 30 7361 (1989)

hv, Et₃NTL 28 4545, 4547 (1987); 30 341, 4113, 7361
(1989); 32 3051 (1991); 36 7877 (1995)Li, NH₃, (NH₄)₂SO₄

JACS 87 1148 (1965)

Na

JOC 46 2622 (1981)

Na, naphthalene

JOC 41 1943 (1976); 46 2622 (1981)

TL 23 5471 (1982); 27 399 (1986); 28 5945 (1987)

JACS 113 5765 (1991)

K, NH₃, (NH₄)₂SO₄

JACS 101 7107 (1979)

Zn, Me₃SiCl

TL 24 2821 (1983); 28 2001 (1987)

(EtO)₃SiH, cat Cp₂Ti(PMe₃)₂

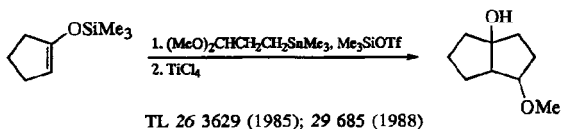
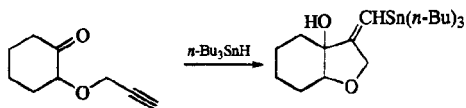
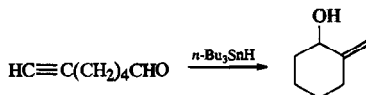
JACS 117 6787 (1995)

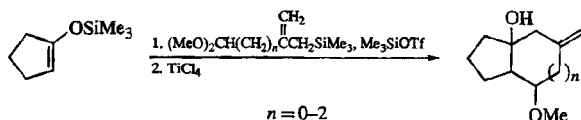
Sml₂

JACS 111 8236 (1989)

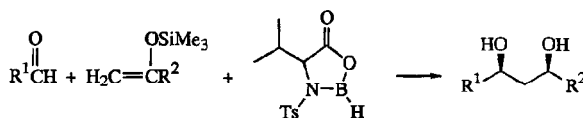
TL 31 4765 (1990)

SL 277 (1995)

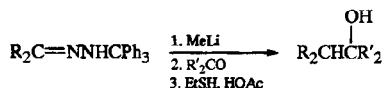




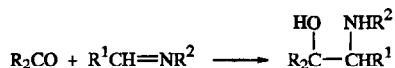
TL 27 5021 (1986); 29 689 (1988)



TL 35 4107 (1994)



CC 22 (1984)


 (indenyl)₂Zr

JACS 113 2321 (1991)

 Cp₂Zr(*n*-Bu)₂

TL 33 4469 (1992)

 NbCl₃(DME)

JACS 109 6551 (1987)


X
Reagent

OR

electrolysis

 TL 32 525 (1991)
 JOC 59 1730 (1994) (inter- and
 intramolecular)

 SmI₂, ROH

 TL 32 3555 (1991)
 JOC 60 6010 (1995) (intra-
 molecular)

n-Bu₃SnH

 TL 35 2205 (1994); 36 253
 (1995) (both intramolecular)

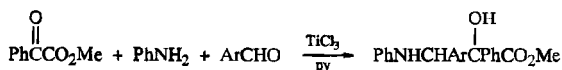
 NMe₂

electrolysis

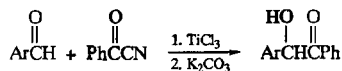
JOC 59 1730 (1994)

 NPh₂

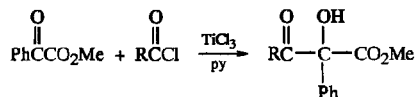
 SmI₂

 JOC 59 6514 (1994)
 JACS 116 7447 (1994) (intra-
 molecular)


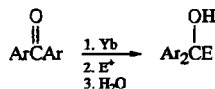
TL 36 5955 (1995)



JOC 58 2889 (1993)



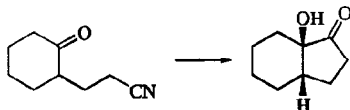
TL 35 2213 (1994)



JOC 53 6077 (1988)



JOC 57 7175 (1992)



electrolysis

TL 31 1303 (1990)

JOC 57 7175 (1992)

Zn, Me₃SiCl, lutidine

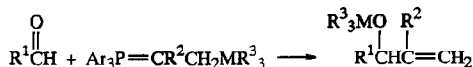
TL 24 2821 (1983)

Zn, Mg, Me₃SiCl

SL 553 (1993)

SmI₂

JOC 54 77 (1989)



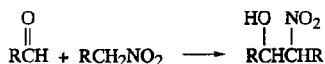
M

Si

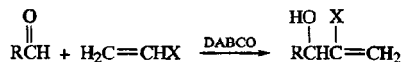
TL 26 4471 (1985); 27 6373 (1986); 28 2379, 4561 (1987)
CC 880 (1986)

Sn

TL 28 4561 (1987)



Amberlyst A21	JOC 59 5466 (1994)
Et ₃ N	TL 35 9293 (intramolecular), 9693 (1994) JOC 60 4196 (1995)
Et ₃ N, pressure	TL 35 8225 (1994)
tetramethylguanidine	JOC 55 3098 (1990)
cat NaOH	Helv 65 1101 (1982) Org Syn Coll Vol 8 332 (1993)
NaOMe	JOC 60 2968 (1995)
KF	TL 3219 (1978); 29 2189 (1988) CL 819 (1983) Chem Pharm Bull 32 2915 (1984) JOC 55 948, 4750 (1990)
KF, cat 18-crown-6	TL 3219 (1978)
KF, <i>n</i> -Bu ₄ NCl	J Carbohydr Chem 1 9 (1982)
KF, <i>n</i> -Bu ₄ NI	BCSJ 59 1753 (1986) JOC 53 281 (1988)
<i>n</i> -Bu ₄ NF·3H ₂ O	TL 29 6083 (1988)
cat <i>n</i> -Bu ₄ NF·3H ₂ O, Et ₃ N, <i>t</i> -BuMe ₂ SiCl	TL 32 3225 (1991)
<i>n</i> -BuLi	Helv 64 2264 (1981); 65 1101 (1982)
<i>n</i> -BuLi / <i>i</i> -PrOTiCl ₃	JOC 54 1233 (1989)
cat [(C ₃ Me ₅)RhCl ₂] ₂	TL 36 6531 (1995)
cat La ₃ (O- <i>t</i> -Bu) ₉ , cat binaphthol (enantioselective)	IACS 114 4418 (1992); 115 10372 (1993)
cat LCl ₃ (L = rare earth), cat binaphthol, base (enantioselective)	TL 34 2657 (1993)
cat La-Li-BINOL	TL 34 851, 855 (1993); 35 6123 (1994) JOC 60 7388 (1995)
cat Sm[N(SiMe ₃) ₂] ₃	JOC 59 2661 (1994)
alumina	Syn 1014 (1983) TL 26 1261 (1985) JOC 55 5159 (1990)



Review: Tetr 44 4653 (1988)

X

CHO

See page 1546, Section 23.

COR

See page 1546, Section 23.

CO₂R

See page 1724, Section 2.

\underline{X} CONH₂

See page 1778, Section 4.

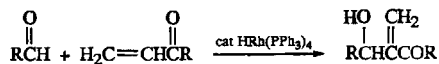
CN

See page 1801, Section 6.

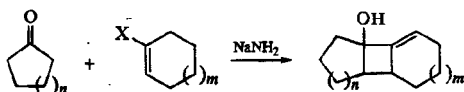
SO₂Ph

TL 27 5095 (1986)

JOC 56 4098 (1991)



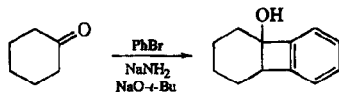
CL 1875 (1985)

 $n = 1-3; m = 1, 2$

Tetr 28 4835 (1972); 30 1237 (1974)

TL 31 7603 (1990)

JOC 58 4572 (1993)



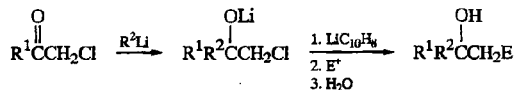
BSCF 302 (1971); 3493 (1973)

Tetr 29 1843 (1973)

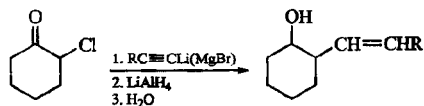
JOC 40 2853 (1975); 51 1419 (1986); 56 4078 (1991)

TL 29 1385 (1988)

3. Alkylation of α -Haloketones

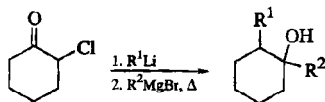
 $\text{E}^+ = \text{D}_2\text{O}, \text{RCHO}, \text{R}_2\text{CO}, \text{CO}_2, \text{O}_2, (\text{MeS})_2$

CC 1153 (1982)



JACS 105 3348 (1983)

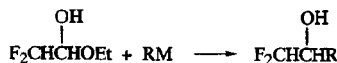
Org Syn 64 10 (1985)



$\text{R}^1 = \text{R}^2 = \text{vinyl}$

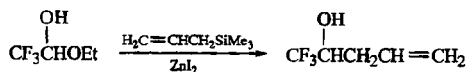
JACS 112 8478 (1990)

4. Addition to Hemiacetals



$\text{RM} = \text{RC}\equiv\text{CLi}$, 1°RMgX , ArMgX , $\text{XZnCHRCO}_2\text{R}$, R_2CHNO_2 (K_2CO_3)

JOC 58 2302 (1993)

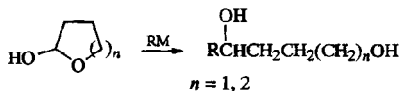


TL 33 1351 (1992)



$\text{R} = \text{vinyl}$ or alkynyl

TL 33 3307 (1992)



$n = 1, 2$

RM

RLi ($\text{R} = \text{Me}$, Ph , alkynyl)

TL 28 423, 6335 (1987); 30 1563 (1989); 32 5143 (1991)

JOC 52 4603 (1987); 54 3370 (1989)

RMgX ($\text{R} = \text{alkyl}$, allyl , aryl , alkynyl , vinyl)

TL 28 423, 6335 (1987); 30 1563 (1989); 32 5143 (1991)

JOC 52 4603 (1987); 54 3370 (1989)

SL 191 (1992)

$\text{HC}\equiv\text{CCH}_2\text{MgX}$

JOC 58 2760 (1993)

Me_3Al

TL 28 6335 (1987)

$\text{Me}_3\text{SiCH}_2\text{CH=CH}_2$, TiCl_4

SL 702 (1991)

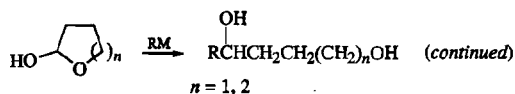
MeTiCl_3

TL 28 6335 (1987)

$\text{RTi}(\text{O-}i\text{-Pr})_3$ ($\text{R} = \text{alkyl}$, alkynyl)

TL 28 423, 6335 (1987); 30 1563 (1989)

JOC 52 4603 (1987); 54 3370 (1989)

RM

RZnX (R = alkyl, alkynyl)

TL 28 423 (1987)

JOC 54 3370 (1989)

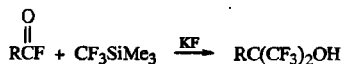
(H₂C=CHCH₂)₂Zn

TL 32 5143 (1991)

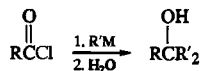
5. Addition to Carboxylic Acids and Derivatives



JACS 68 1382 (1946)



JOC 57 1124 (1992)

R'M

RC≡CMgX

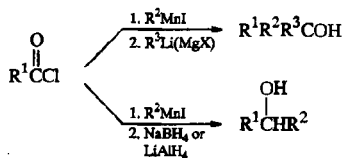
TL 36 119 (1995)

H₂C=C=CHB (alkyne product)

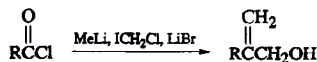
JOC 60 544 (1995)

RMnI

Can J Chem 58 287 (1980)

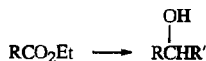


TL 27 4441 (1986)



JCS Perkin I 77 (1989)

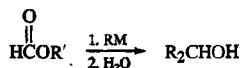
JOC 59 332 (1994)

*i*-Bu₂AlH / R'Li

TL 31 4985 (1990)

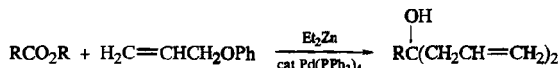
JOC 57 5469, 5947 (1992)

$i\text{-Bu}_2\text{AlH} / \text{R}'\text{MgX}$	JOC 48 2775 (1983); 56 2107, 4370 (1991); 57 5947 (1992) TL 28 3905 (1987); 31 4985 (1990); 32 5329 (1991); 34 3985 (1993) SL 613 (1995)
$i\text{-Bu}_2\text{AlH} / n\text{-Bu}_3\text{SnCH}_2\text{CH}=\text{CH}_2$, Lewis acid	TL 34 5729, 5777 (1993)
$i\text{-Bu}_2\text{AlH} \cdot i\text{-Bu}_3\text{Al} / \text{R}'\text{Li}$ or $\text{R}'\text{MgX}$	JOC 57 5469 (1992); 59 4596 (1994) SL 552 (1995)
$\text{R}'\text{MgX}$, LiBH_4	TL 25 1321 (1984); 28 3905, 4143 (1987); 32 3957 (1991)
$2 \text{ R}'\text{MgX}$, Cp_2TiCl_2	TL 21 2175 (1980)



RM

ArLi	JOC 47 4347 (1982); 59 7701 (1994) JACS 116 7072 (1994)
ArMgX	JOC 57 4421 (1992)
$\text{RC}\equiv\text{CMgX}$	TL 36 119 (1995)



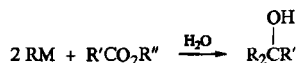
TL 34 7619 (1993)



$\text{R} = 1^\circ, 2^\circ$ alkyl; allyl; aryl

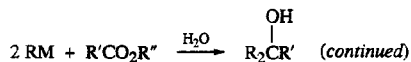
JCS D 1160 (1970)

Org Syn Coll Vol 6 240 (1988)



RM

MeLi	JOC 53 1040 (1988) (4-alkanolide); 57 1047 (1992) (5-alkanolide)
$\text{CF}_3\text{CF}_2\text{Li}$	JOC 52 2481 (1987)
$\triangle\text{-Li}$	JOC 57 6431 (1992); 58 1639 (1993)
ArLi	JACS 108 3762 (1986); 117 11205 (1995) JOC 60 1755 (1995)
$\text{RCH}=\text{CRLi}$	JOMC 136 1 (1977) JACS 114 6942 (1992) Org Syn Coll Vol 8 505 (1993)

RM

RC≡CLi

TL 937 (1978)

IOC 59 5292 (1994)

RMgX

M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances," Prentice Hall, New York (1954), pp 549-708 (review)

Org Syn Coll Vol 3 839 (1955)

IACS 108 4119 (1986); 111 4392 (1989); 114

4128 (1992)

JOC 52 4511 (1987) (5-alkanolide); 58 3748 (1993);

59 4680 (1994); 60 3155 (1995)

TL 35 8533 (1994)

Me₄CoLi₂

TL 31 511 (1990)

RCeCl₂

IACS 111 4392 (1989)

Me₃SiCH₂MgCl, CeCl₃

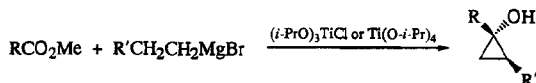
TL 28 6261 (1987)

EtMgBr, (n-BuO)₃VO

Russ J Chem 29 66 (1993)

CH₂I₂, Sm

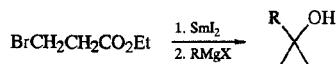
TL 30 5149 (1989)



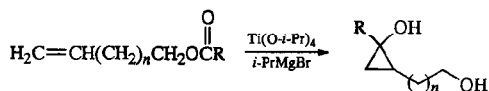
IOC USSR 25 2027 (1989); 27 250, 1249 (1991)

JOC 58 502 (1993)

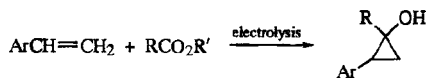
JACS 116 9345 (1994); 117 9919 (1995)



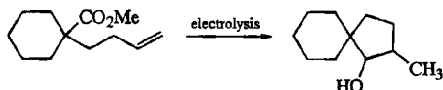
TL 32 7691 (1991)

 $n = 1, 2$

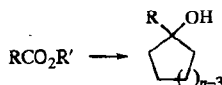
TL 36 6079 (1995)



JOC 57 5561 (1992)



JOC 57 1061 (1992)



Reagent(s)

Br(CH₂)₅Br, Li, ultrasound

ת

TL 28 2013 (1987)

$$\text{BrMg-C}_n\text{-MgBr}$$

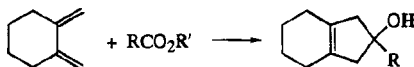
4.5

Compt Rend 144 1358 (1907)

JACS 72 3483 (1950); 74 5498 (1952)

TL 22 4995 (1981); 31 6067 (1990)

JOC 51 2147 (1986); 52 4025 (1987); 60 3448 (1995)

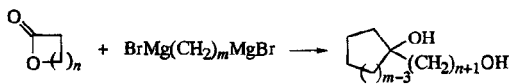


electrolysis

JOC 57 5561 (1992)

Mg

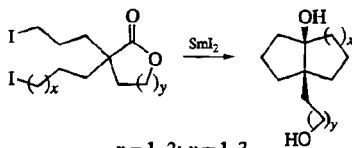
JACS 114 4415 (1992); 117 5429 (1995)


$$n = 1-4; m = 4, 5$$

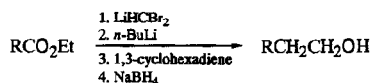
JOC 45 1828 (1980); 52 569 (1987)

Tetr 40 865 (1984)

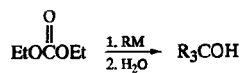
TL 28 4997 (1987)

 $x = 1, 2; y = 1-3$

JACS 117 3705 (1995)



JACS 108 1324 (1986)

RM

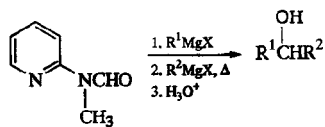
RLi

JOC 55 3697 (1990); 57 61 (1992)

RMgX

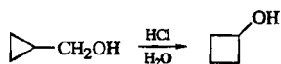
Org Syn Coll Vol 2 602 (1943)

JOC 55 3697 (1990)

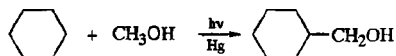


TL 22 1085 (1981)

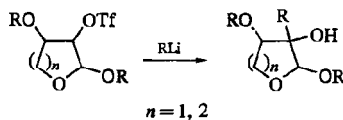
10. MISCELLANEOUS REACTIONS



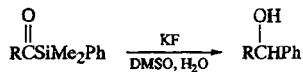
Tetr 11 171 (1960)
Org Syn Coll Vol 7 114, 117 (1990)



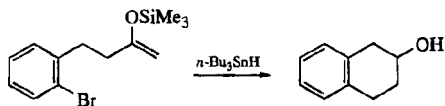
CC 970 (1987)
TL 28 5599 (1987)



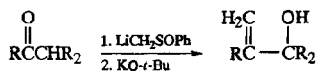
TL 36 7665 (1995)



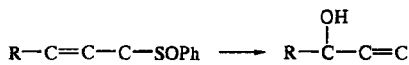
TL 36 5555 (1995)



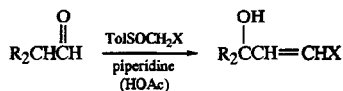
TL 27 1355 (1986)



Syn 640 (1980)



See page 234, Section 6 and page 351, Section 1.



X

CO₂R

See page 1711, Section 1.

CN

See page 1711, Section 1.

SOAr

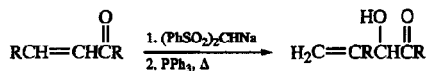
TL 36 4889 (1995)

SO₂Ar

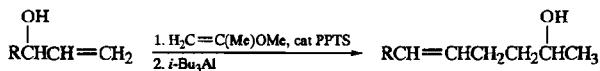
TL 31 2487 (1990)

Tetr 46 7197 (1990)

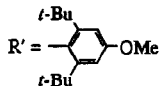
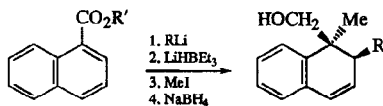
IOC 56 3189 (1991); 57 3857 (1992); 58 1596 (1993); 60 6000 (1995)



TL 33 4913 (1992)



IOC 60 4318 (1995)



IOC 55 2276 (1990)

ALDEHYDES AND KETONES

GENERAL REFERENCES

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Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VII/1, G. Thieme, Stuttgart (1954)
(aldehydes)

Quart Rev 20 169 (1966) (aldehyde synthesis)

"The Chemistry of the Carbonyl Group," Ed. S. Patai, Interscience, New York (1966)

C. D. Gutsche, "The Chemistry of Carbonyl Compounds," Prentice Hall, Englewood Cliffs, New Jersey
(1967)

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(ketones)

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(ketones)

Syn 633 (1979) (synthesis of aldehydes, ketones and carboxylic acids from lower carbonyl compounds by
C-C coupling reactions)

Tetr 36 2531 (1980) (carbonyl homologation and masked homoenolate equivalents)

Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E3, G. Thieme, Stuttgart-New York (1983)
(aldehydes)

"The Chemistry of Enones," Parts 1 and 2, Eds. S. Patai and Z. Rapoport, J. Wiley, Chichester, U. K. (1989)

1. CARBONYL TRANSPOSITION



PhCHO, OH⁻ / LiAlH₄, AlCl₃ / O₃

CC 898 (1967)
JCS C 244 (1970)

PhCHO, OH⁻ / NaBH₄ / Ac₂O / O₃ / Li, NH₃

JACS 104 1907 (1982)

t-BuONO₂, KO-*t*-Bu / NaBH₄ / Zn, HOAc

JOC 33 1733 (1968)

AmONO, KO-*t*-Bu / N₂H₄, KOH / NaHSO₃

CC 1350 (1968)

LiN(*i*-Pr)Cy / (PhS)₂ / NaBH₄ / MsCl-py or TsOH /
HgCl₂-H₂O or TiCl₄-HOAc

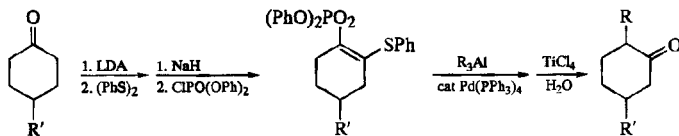
JACS 97 438 (1975)

TsNHNH₂ / 2 *n*-BuLi / (MeS)₂ / *n*-BuLi / NH₄Cl /
H₂O, HgCl₂

TL 531 (1979)
CL 931, 1099 (1980)

PhSO₂NHNH₂ / 2 *n*-BuLi / Me₃SiCl / *m*-
ClC₆H₄CO₂H / LiAlH₄ / Na₂Cr₂O₇, H₂SO₄

JOC 43 1620 (1978); 45 3028 (1980)



TL 22 1609 (1981)

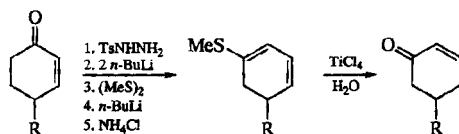


H₂O₂, NaOH / N₂H₄·H₂O, HOAc / PCC

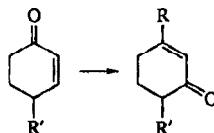
JACS 111 3707 (1989)

H₂O₂, NaOH / NaBH₄, CeCl₃ / CBr₄,
PPh₃ / Zn, CuI, ultrasound / MnO₂

JOC 57 2757 (1992)



CL 1099 (1980)



RLi/PCC

Syn Commun 6 649 (1976)

JOC 42 682, 813 (1977); 50 2557 (1985); 51 4497 (1986); 56 1481 (1991); 58 3923 (1993)

JACS 105 7352 (1983); 110 1901 (1988)

CC 358 (1987)

RLi/PCC, SiO₂, (ultrasound)

JOC 58 2966 (1993)

RLi/CrO₃, H₂SO₄

JOC 36 2021 (1971); 39 2317 (1974); 56 1481 (1991)

Syn Commun 11 7 (1981)

RLi/PhSeCl/(PhS)₂/H₂O, HgCl₂

JACS 97 4018 (1975)

RLi/PhSeCl/O₃/Hg(OAc)₂ or HCl or HCO₂H

JOC 45 2551 (1980), 47 1258 (1982)

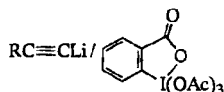
RCH=CHLi(MgX)/PDC

TL 30 1033 (1989)

RC≡CLi/PDC

TL 28 1069 (1987)

JACS 113 1355 (1991)



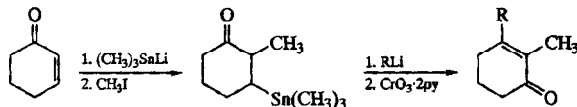
JACS 113 1355 (1991)

RMgX/PCC

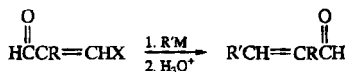
JACS 108 3443 (1986)


RMgX/CrO₃, H₂SO₄

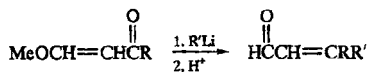
JACS 108 3385 (1986)



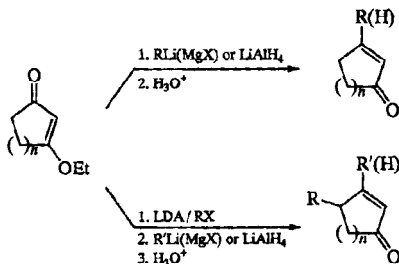
JACS 99 4836 (1977)



<u>X</u>	<u>R'M</u>	
OEt		Ber 115 3898 (1982) Angew Int 19 816 (1980)
NMe ₂	R'Li	JOC 51 879, 1631 (1986)



JOC 51 4743 (1986)

 $n = 0, 1, 2$

JACS 72 1645 (1950); 102 782 (1980); 103 82 (1981); 105 1292 (1983); 106 2115, 3353 (1984); 107 268, 7732, 7745 (1985); 108 806, 1106, 3110, 6276 (1986); 109 4690, 5491 (1987); 111 5312 (1989); 112 9292 (1990); 114 5959, 7375 (1992)

JCS 1779 (1953)

JOC 38 1451, 1775 (1973); 43 3968 (1978); 46 2400 (1981); 47 381, 3297, 4820, 5096 (1982); 48 2318 (1983); 49 2152 (1984); 50 3155, 5550, 5727 (1985); 51 879, 1490, 4323 (1986); 52 120, 3491 (1987); 53 2560, 3823, 4314, 4945 (1988); 56 3973, 3988, 5572 (1991); 57 1151 (1992); 58 1900, 3877 (1993)

Syn Commun 6 555 (1976); 7 409 (1977); 12 167, 521 (1982)

TL 22 15, 97 (1981); 23 3283 (1982); 27 2087, 5232 (1986); 28 1329, 3065, 3107 (1987); 30 4045 (1989); 31 2239 (1990)

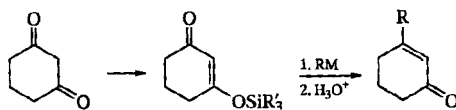
Tetr 38 3527 (1982)

Can J Chem 60 2965 (1982)

Org Syn 64 68, 73 (1985)

CC 75 (1986)

Org Syn Coll Vol 7 241 (1990)

RM

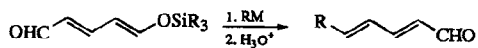
RLi

Syn Commun 12 795 (1982)

TL 30 3327 (1989)

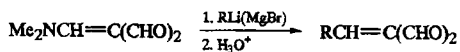
RLi, CeCl₃

TL 30 3327 (1989)

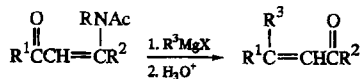


RM = *n*-BuLi; 1°, 2° RMgX; PhCH₂MgCl; ArMgX

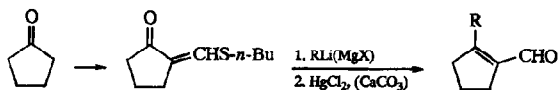
SL 898 (1991)



TL 29 2861 (1988)



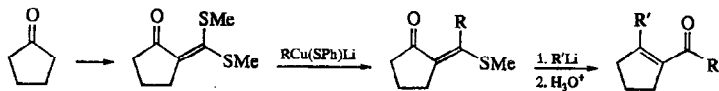
Heterocycles 19 1211 (1982)



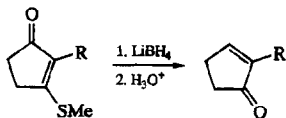
TL 1015 (1979)

JACS 113 3873 (1991)

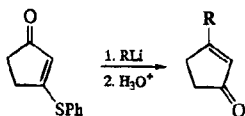
JOC 58 600 (1993)



TL 23 3751 (1982)



TL 23 561 (1982)

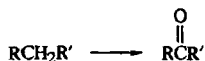


Organomet 1 1240, 1243 (1982)

JOC 52 110 (1987)

2. OXIDATION

1. Alkanes



O₂, cat Co Schiff base, Me₂CHCHO

TL 36 8497 (1995)

O₃, SiO₂

Angew Int 15 761 (1976)

Ber 118 2429 (1985)



JOC 58 5548 (1993)



JACS 111 6749 (1989)

CH₃CO₃H, cat Ru-C

TL 35 7953 (1994)

NaIO₄, cat RuCl₃·H₂O

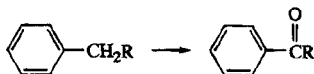
CL 1385 (1985) (R = cyclopropyl)

H₂SO₄

Org Syn Coll Vol 6 48 (1988)

Beauveria sulfurescens (enantioselective)

JOC 57 7212 (1992)



(R = H or alkyl)

CrO₂Cl₂, (ultrasound)/Zn

JOC 58 512 (1993)

CrO₃, HOAc



JCS 727 (1940)

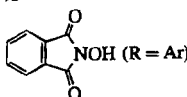
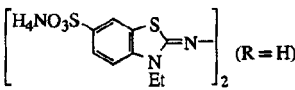
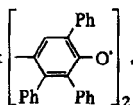



JACS 69 576 (1947)

Tetr 20 409 (1964)

Ind J Chem 2 229 (1964)

JCS C 2603 (1968); 1240 (1969)

	Acta Chem Scand 24 2252 (1970) Steroids 18 593 (1971); 22 327 (1973) Org Prep Proc Int 4 67 (1972) Syn Commun 3 89 (1973) JOC 39 1416 (1974); 46 1752 (1981); 50 2435 (1985); 59 5445 (1994)
CrO_3 , Ac_2O	Helv 64 599 (1981) JOC 59 7785 (1994)
CrO_3 , H_2SO_4 , H_2O , CH_3COCH_3	JCS C 2603 (1968); 1240 (1969) JOC 50 2435 (1985)
CrO_3 , 3,5-dimethylpyrazole	JACS 108 3040 (1986) JOC 56 2040 (1991)
CrO_3 , HCl , bipy	JOC 50 2435 (1985)
cat CrO_3 , <i>t</i> -BuO ₂ H	TL 28 2131 (1987) J Mol Catal 66 155 (1991) JOC 58 4871 (1993)
cat  CrO_2 , <i>t</i> -BuO ₂ H	Bull Soc Chim Belg 94 651 (1985) TL 27 3139 (1986)
PCC, Celite	Syn Commun 16 1493 (1986) JOC 57 4074 (1992); 58 4871 (1993)
PCC, <i>t</i> -BuO ₂ H, Celite	JOC 52 5048 (1987)
cat Cr-pillared montmorillonite, <i>t</i> -BuO ₂ H	JOC 57 5841 (1992)
cat $\text{Cr}(\text{CO})_6$, <i>t</i> -BuO ₂ H	JOC 50 2791 (1985); 59 5445 (1994)
cat $(n\text{-Bu}_3\text{SnO})_2\text{CrO}_2$, $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$, cat Adogen 464 [®] , cat TsOH	TL 36 5735 (1995)
KMnO_4 , KOH , $(n\text{-Bu}_4\text{N})\text{HSO}_4$	JOC 59 8220 (1994)
cat $\text{RuCl}_2(\text{PPh}_3)_3$, <i>t</i> -BuO ₂ H	TL 34 1299 (1993)
$\text{Ce}(\text{O}_3\text{SCH}_3)_2(\text{OH})_2 \cdot \text{H}_2\text{O}$, $\text{CH}_3\text{SO}_3\text{H}$	JOC 54 1526 (1989)
$\text{Ce}(\text{O}_3\text{SCH}_3)_3 \cdot 2\text{H}_2\text{O}$, electrolysis	TL 28 1067 (1987) (ArCHO > ArCOR) JOC 54 1526 (1989)
CAN	TL 4493 (1966); 36 4345 (1995) JOC 31 2033 (1966); 58 7149 (1993); 59 878 (1994)
CuSO_4 , $\text{K}_2\text{S}_2\text{O}_8$, H_2O	TL 22 2605 (1981) (electron-rich arenes) JOC 57 2774 (1992)
KO_2 , <i>o</i> -NO ₂ C ₆ H ₄ SO ₂ Cl	TL 30 6357 (1989)
<i>t</i> -BuO ₂ H, cat $\text{C}_6\text{F}_5\text{SeO}_2\text{H}$ (R = Ar)	TL 35 5149 (1994)
$\text{PhI}(\text{OAc})_2$, cat  SeO_2O (R = Ar)	TL 35 5149 (1994)

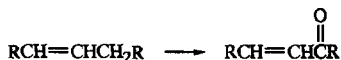
- (PhSeO)₂O TL 3331 (1979)
- O₂, cat  (R = Ar) JOC 60 3934 (1995)
- O₂, cat laccase, cat JOC 60 4320 (1995)
-  (R = H)
- O₂, hv, cat 9,10-dicyanoanthracene, cat FeCl₂, cat methylviologen TL 32 4291 (1991)
- O₂, Me₂CHCHO, cat Co catalyst SL 189 (1995)
- O₂, cat ClRh(PPh₃)₃ TL 3665 (1967); 2917 (1968)
- O₂, cat CuCl, cat  , butyronitrile TL 35 5833 (1994)
-  cat Ru porphyrin JACS 114 10660 (1992)
- DDQ Syn 144 (1979)
- JOC 48 749 (1983); 53 4253, 4587 (1988); 54 2170 (1989)
- TL 29 3207 (1988)
-  JACS 116 2375 (1994)
-  JACS 111 6749 (1989); 116 2375 (1994)
- NBS/H₂O, AgNO₃ JACS 116 11275 (1994)
- NaBr, NaOCl, (n-Bu₄N)HSO₄ (R = Ar) JOC 57 4555 (1992)
- chloroperoxidase JACS 117 10419 (1995)


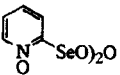
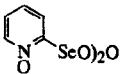

2. Alkenes

See also page 638, Section 4.



- SeO₂ Org Rxn 24 261 (1976) (review)
JACS 112 775 (1990)
- C₆F₅SeO₂H TL 35 5149 (1994)

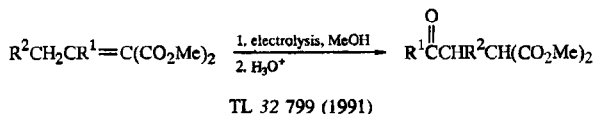
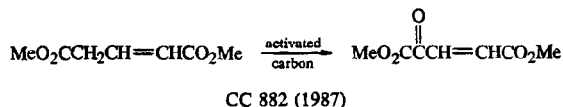


- O_2 , hv, tetraphenylporphine, Ac_2O , py, DMAP JOC 48 4135 (1983)
- O_2 , , cat Co Schiff base TL 35 4003 (1994)
- O_2 , cat $\text{CoBr}_2(4\text{-MeC}_5\text{H}_4\text{N})_2$ TL 35 4461 (1994)
- SeO_2 Tetr 6 217 (1959)
 CC 1277 (1968)
 JACS 92 3429 (1970); 93 4835, 5311 (1971); 112 462 (1990) (on enol silane)
 Org Rxs 24 261 (1976) (review)
- $\text{C}_6\text{F}_5\text{SeO}_2\text{H}$ TL 35 5149 (1994)
- $t\text{-BuO}_2\text{H}$, cat $\text{C}_6\text{F}_5\text{SeO}_2\text{H}$ TL 35 5149 (1994)
-  TL 35 5149 (1994)
- $\text{PhI}(\text{OAc})_2$, cat  TL 35 5149 (1994)
- PhIO_2 ,  Tetr 41 4359 (1985)
 JOC 53 3912 (1988)
- $t\text{-BuO}_2\text{H}$, cat $\text{Cr}(\text{CO})_6$ TL 25 1235 (1984); 31 2239 (1990)
 JCS Perkin I 267 (1985)
- $t\text{-BuO}_2\text{H}$, PCC, Celite JOC 52 5048 (1987)
- $t\text{-BuO}_2\text{H}$, cat CrO_3 TL 28 4665 (1987); 30 6577 (1989)
- Na_2CrO_4 , HOAc, Ac_2O JOC 35 192, 4068 (1970); 55 1598 (1990)
 IACS 106 6690 (1984); 110 5806 (1988)
- K_2CrO_4 , HOAc, Ac_2O JOC 55 1598 (1990)
- CrO_2Cl_2 , $t\text{-BuOH}$, 3,5-dimethylpyrazole JOC 57 922 (1992)
- $t\text{-C}_4\text{H}_9\text{OCrO}_3\text{H}$ JOC 34 3587 (1969)
- CrO_3 , $t\text{-BuOH}$ JACS 79 6308 (1957)
 Helv 35 284 (1962)
- CrO_3 , py, Celite JOC 52 3346 (1987)
- CrO_3 , py, molecular sieves JOC 54 1468 (1989)
- $\text{CrO}_3 \cdot 2\text{py}$ JOC 34 3587 (1969); 52 3573 (1987); 57 4591 (1992)
 Syn Commun 6 217 (1976)
 JACS 107 7724 (1985); 108 6276 (1986)

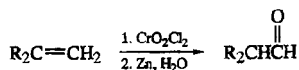
CrO ₃ ·1py	J Chem Res (S) 42 (1979)
CrO ₃ ·3,5-dimethylpyrazole	JOC 43 2057 (1978); 52 1686, 2960 (1987); 53 3912 (1988); 54 1483 (1989); 57 4043 (1992); 58 4871 (1993) JACS 108 2090, 3513 (1986); 110 4041, 8483 (1988); 113 3533, 5765 (1991) TL 27 3411, 5245 (1986); 29 4959 (1988)
CrO ₃ , HOAc	JACS 63 758 (1941) BCSJ 52 184 (1979) TL 29 6779 (1988)
CrO ₃ , HOAc, Ac ₂ O	BCSJ 52 184 (1979) (4-oxo-2-alkenoates) JOC 47 5093 (1982) (4-oxo-2-alkenoates)
NBS, H ₂ O, THF	JOC 60 833 (1995)



NaO ₂ , H ₂ O, EtOH	TL 22 5127 (1981)
VO(OR')Cl ₂ , ROH (R' = Et, <i>i</i> -Pr)	TL 32 1741 (1991)
tetrazolium salt, KOH	TL 28 4323 (1987)



BH ₃ ·SMe ₂ /PCC	JOMC 172 C20 (1979) Tetr 42 5515 (1986)
ClBH ₂ ·SMe ₂ /PCC	Tetr 42 5515 (1986) SL 503 (1992)
Me ₂ CHCMe ₂ BHCl·SMe ₂ /PCC	Tetr 42 5515 (1986)
(Sia) ₂ BH/PCC	Syn 151 (1980) Tetr 42 5515 (1986) JOC 59 4760 (1994)
PhSH, AIBN/NCS/CuO, CuCl ₂ , H ₂ O	JOC 41 3261 (1976)
O ₂ , cat PdCl ₂ , cat CuCl	JOC 60 4678 (1995)
O ₂ , cat PdCl ₂ , CuCl	TL 27 5955 (1986)

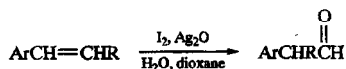


JOC 33 3970 (1968)

Org Syn 51 4 (1971)

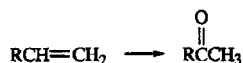
Org Syn Coll Vol 6 1028 (1988)

TL 31 6839 (1990)



CL 341 (1984)

SL 555 (1993)

cat $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, cat $\text{Cu}(\text{ClO}_4)_2(\text{HMPA})_4$, O_2 IACS 100 5437 (1978)cat $(\text{RhO}_2\text{L}_4)\text{X}$ ($\text{L} = \text{Ph}_3\text{As}$, PhAsMe_2 ; $\text{X} = \text{ClO}_4$, PF_6), O_2 Nouv J Chim 4 161 (1980)

cat PdCl_2 , CuCl or CuCl_2 , O_2

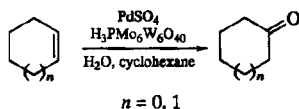
Angew Int 1 80 (1962) (review)
 JOC 29 241 (1964); 39 3276 (1974); 52 4592 (1987);
 60 4678 (1995)
 TL 2975 (1976); 21 955 (1980); 27 2529, 4431
 (1986); 34 5871 (1993); 36 5379 (1995)
 JACS 101 5070, 5072 (1979); 105 7352 (1983); 108
 3474 (internal alkene), 8015 (1987); 111 1396
 (1989)
 Syn Commun 10 273 (1980)
 Topics Curr Chem 91 29 (1980) (review)
 Syn 369 (1984) (review)
 Israel J Chem 24 153 (1984)
 CC 1578 (1987)
 Org Syn Coll Vol 7 137 (1990); 8 208 (1993)
 SL 875 (1991)
 "Comprehensive Organic Synthesis," Eds. B. M.
 Trost and I. Fleming, Pergamon, Oxford (1991),
 Vol 7, Part 3.4, p 449 (review)

cat PdCl_2 , CuCl_2 , O_2 , PEG-400 TL 26 2263 (1985)cat PdCl_2 , CuCl_2 , H_2O , C_6H_6 , $(n\text{-C}_{16}\text{H}_{33}\text{NMe}_3)\text{Br}$ TL 24 5159 (1983)cat $\text{Pd}(\text{OAc})_2$, H_2O_2 JOC 45 5387 (1980)cat $\text{Pd}(\text{OAc})_2$, cat benzoquinone, electrolysis TL 28 3683 (1987)cat $\text{Pd}(\text{OAc})_2$, cat benzoquinone, HClO_4 JOC 55 2924 (1990)

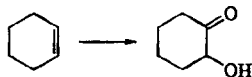
TL 35 6481 (1994)

cat $\text{Pd}(\text{OAc})_2$, cat hydroquinone, cat $\text{Fe}(\text{II})$
 phthalocyanine, O_2 TL 29 2885 (1988)
 JACS 112 5160 (1990)

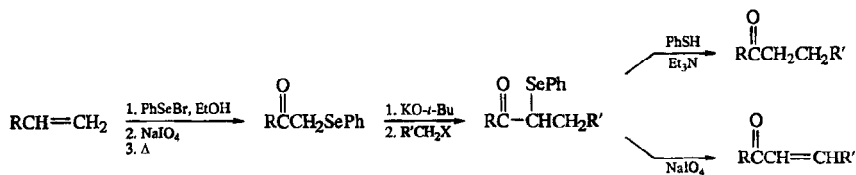
- cat Pd(DBA)₂, cat AgNO₂, O₂ TL 30 6319 (1989)
 cat PdSO₄, cat CuSO₄, cat H₃PV₆Mo₆O₄₀,
 cyclodextrin TL 36 387 (1995)
 Hg(OAc)₂, H₂O/Li₂PdCl₄ TL 34 5871 (1993)
 Hg(OAc)₂, CH₃OH / cat Li₂PdCl₄, CuCl₂ CC 818 (1971)
 cat Hg(O₂CEt)₂, CrO₃ or Na₂Cr₂O₇, H₃O⁺ JOC 40 3577 (1975)
 Syn Commun 11 7 (1981)



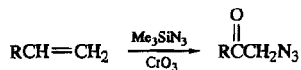
CC 1274 (1981)



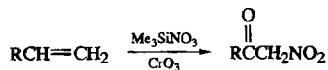
See page 978, Section 3.



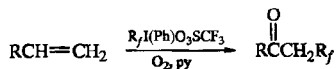
TL 799 (1978)



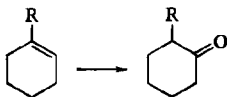
TL 36 6753 (1995)



TL 36 7149 (1995)



TL 23 4101 (1982)



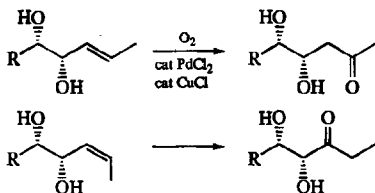
$\text{BH}_3/\text{H}_2\text{CrO}_4$

JACS 83 2951 (1961)

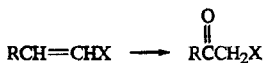
JOC 50 2179 (1985)

$\text{ClBH}_2\cdot\text{SMe}_2/\text{PCC}$

Tetr 42 5515 (1986)



JOC 60 4678 (1995)



X

Oxidant

CH_2OR , CH_2OAc

benzoquinone or $\text{O}_2\text{-CuCl}$,
cat PdCl_2

TL 23 2679 (1982)

CH_2COCH_3 , $\text{CH}_2\text{CO}_2\text{R}$

O_2 , CuCl , cat PdCl_2

CL 859 (1982)

COR , CO_2R

H_2O_2 or $t\text{-BuO}_2\text{H}$, cat Na_2PdCl_4

CL 257 (1980)



KMnO_4 , Ac_2O

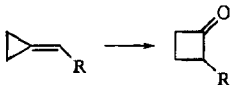
JACS 93 3303 (1971)

JOC 39 2314 (1974); 41 1903 (1976)

TL 31 3409 (1990)

KMnO_4 , $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$

JOC 54 5182 (1989)

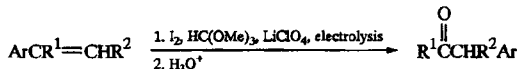


$m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$

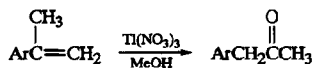
TL 29 27 (1988)

$t\text{-BuO}_2\text{H}$, dialkyl tartrate, $\text{Ti}(\text{O-}i\text{-Pr})_4$, molecular
sieves

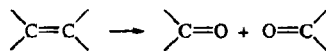
TL 35 6499 (1994)



TL 30 5309 (1989)



JOC 53 3761 (1988)



aldehydes and/or ketones

Reviews:

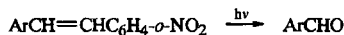
Chem Rev 58 925 (1958) (ozonolysis)

Acct Chem Res 1 313 (1968) (ozonolysis mechanism)

Russ Chem Rev 50 636 (1981) (ozonolysis)

W. Carruthers, "Some Modern Methods of Organic Synthesis," Cambridge Univ Press (1986), Third Ed., Chpt 6

O_3/H_2 , cat Pd-C	Tetr 2 203 (1958); 3 230 (1958) JOC 59 5055 (1994)
O_3/Zn , HOAc	JACS 77 1212 (1955); 108 4603 (1986) JOC 59 5055 (1994)
O_3/I^- , HOAc	Org Syn 41 41 (1961)
$\text{O}_3/\text{Me}_2\text{S}$	TL 4273 (1966); 1391 (1969); 2417 (1973) JACS 108 1039, 1239 (1986) JOC 52 1603 (1987)
$\text{O}_3/\text{SC}(\text{NH}_2)_2$	Tetr 38 3013 (1982)
$\text{O}_3/n\text{-Bu}_3\text{P}$	JOC 58 5931 (1993)
$\text{O}_3/\text{Ph}_3\text{P}$	JOC 30 1976 (1965); 58 6857 (1993); 59 5055 (1994)
$\text{O}_3/(\text{MeO})_3\text{P}$	JOC 25 2703 (1963) JACS 108 1039 (1986)
O_3/py	JACS 80 915 (1958) Compt Rend 250 1078 (1960)
KMnO_4	JOC 51 3213 (1986)
KMnO_4 , alumina, H_2O	JOC 58 2918 (1993)
NaIO_3 , cat $(n\text{-Bu}_4\text{N})_5(\text{H}_2\text{O})\text{RuSiW}_{11}\text{O}_{39}$, electrolysis	SL 139 (1992)
NaIO_4 , cat KMnO_4	Can J Chem 33 1710, 1714 (1955)
NaIO_4 , cat $\text{RuCl}_3 \cdot (\text{H}_2\text{O})_n$	JOC 51 3247 (1986)
NaIO_4 , cat RuO_2	JOC 52 2875 (1987); 55 3568 (1990)
NaIO_4 , cat OsO_4	Soc Chem Ind 62 90 (1943) JOC 21 478 (1956) JACS 108 4149 (1986)
NaIO_4 , cat OsO_4 , NMO	TL 28 3225 (1987)
$(\text{bipy})\text{H}_2\text{CrOCl}_5$	Org Prep Proc Int 14 362 (1982) (aryl alkenes)
$\text{R}_2\text{C}=\text{CHR} \longrightarrow \text{R}_2\text{C}=\text{O} + \text{RCO}_2\text{H}$	
H_2CrO_4 , cat OsO_4	JOC 58 4745 (1993)
KMnO_4 , NaIO_4	Can J Chem 33 1714 (1955) Syn Commun 12 1063 (1982)
KMnO_4 , silica gel	JOC 52 3698 (1987)



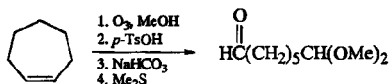
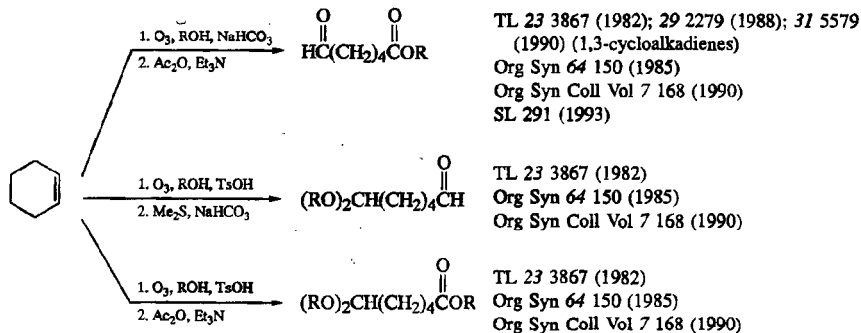
SL 215 (1990)

 $\text{O}_2, h\nu$

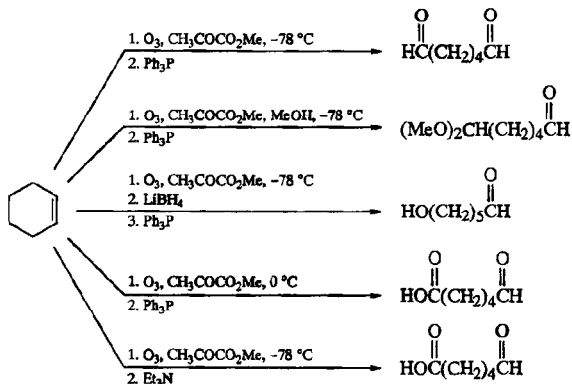
TL 34 4341 (1993)

 $\text{CrO}_3, \text{Me}_3\text{SiCl} (\text{R} = \text{H}, \text{Ar})$

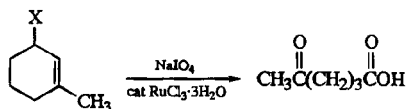
TL 30 193 (1989)



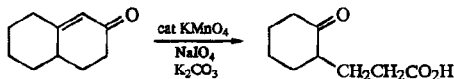
JACS 110 6210 (1988)



TL 34 6591 (1993)

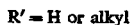


JOC 52 689 (1987)

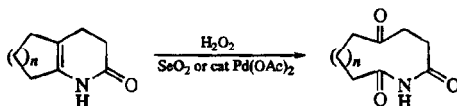


Can J Chem 39 599 (1961)

Org Syn Coll Vol 6 690 (1988)



TL 31 4991 (1990)



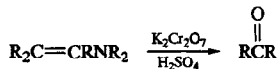
TL 34 4843 (1993)

3. Enamines

See also page 1259, Section 30, and page 1259, Section 31.



TL 35 219 (1994)



TL 36 2921 (1995)

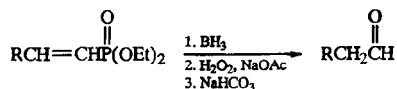


TL 25 3743, 3747 (1984)

JACS 107 1444 (1985); 111 371 (1989)

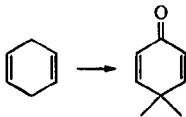
JOC 54 6012 (1989)

4. Alkenylphosphonates



JACS 113 7424 (1991)

5. Dienes and Polyenes

*t*-BuO₂H, PDC

TL 29 3907 (1988)

JOC 57 6037 (1992)

PDC

TL 27 1481 (1986)

JACS 109 3991 (1987); 110 5547 (1988)

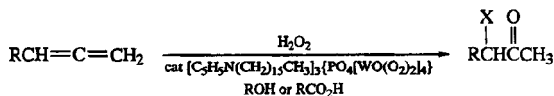
Na₂CrO₄, HOAc, Ac₂O

JACS 109 3991 (1987)

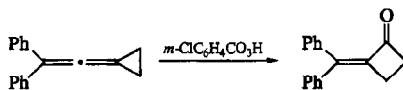
CrO₃, HOAc, Ac₂O

JACS 109 3991 (1987)

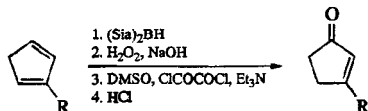
JOC 52 5482 (1987)

X = OR, O₂CR

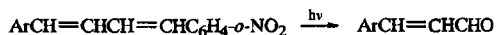
JOC 59 5681 (1994)



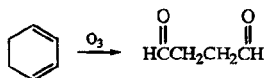
TL 33 2539 (1992)



JOC 55 3395 (1990)

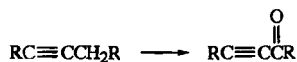


SL 215 (1990)



JACS 110 4735 (1988)

6. Alkynes

*t*-BuO₂H, 0.5 SeO₂

JACS 99 5526 (1977)

JOC 44 4202 (1979)

t-BuO₂H, cat CrO₃, TsOH

TL 29 2321 (1988)

CrO₃·2py

TL 4379 (1971)

JOC 44 4075 (1979)

PCC

JOC 44 4075 (1979)



R = H or R'; R' = H or R

BH₃ or R₂BH/H₂O₂, NaOH or NaOAc

JACS 83 3834 (1961); 89 5086 (1967); 91 4771 (1969); 111 6676 (1989)

Org Rxs 13 1 (1963) (review)

TL 41 (1970); 29 1895 (1988); 30 6487 (1989)

(1,3-diyne)

Organomet Chem Syn 1 249 (1971)

9-BBN/H₂O₂, NaOH, NaH₂PO₄

JACS 101 96 (1979)

ClBH₂/H₂O₂, NaOH or NaOAc

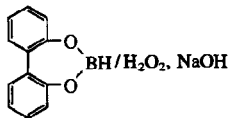
JOC 38 1617 (1973)

Me₂CHCMe₂BHX·SMe₂ (X = Cl, Br, I)/H₂O₂, NaOH

TL 34 5113 (1993)

Br₂BH·SMe₂/H₂O₂, NaOH

JOC 45 389 (1980)

BH/H₂O₂, NaOH

Heterocycles 32 425 (1991)

CB/H₂O₂, NaOH

JACS 94 4370 (1972); 97 5249 (1975)

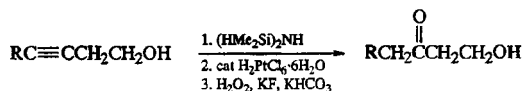
HSiMe(OEt)₂, cat ClRh(PPh₃)₃/Me₃NO, KHF₂ (R' = H)

TL 27 75 (1986)

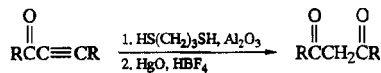
H₅IO₆, NaHSO₃

JOC 59 5550 (1994)

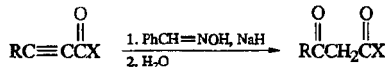
cat $\text{PdCl}_2(\text{CH}_3\text{CN})_2$, H_2O , ultrasound	TL 28 3127 (1987) (alkynone to 1,4- and 1,5-diketones)
cat PtX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), H_2O , THF	JOC 58 7613 (1993)
cat $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, H_2O , MeOH	JOC 56 3729 (1991)
cat $\text{NaAuCl}_4 \cdot 2\text{H}_2\text{O}$, H_2O , ultrasound	TL 28 3127 (1987) (alkynone to 1,5-diketone)
HCO_2H	JOC 56 2912 (1991); 58 7434 (1993)
HCl , H_2S	JOC 54 1218 (1989)
H_2O , H_2SO_4 , $\text{Hg}(\text{II})$	JCS 3257 (1954) JACS 76 524 (1954); 86 935, 936 (1964) (both alkynone to 1,4- and 1,5-diketones) Can J Chem 50 1105 (1972) JOC 40 2250 (1975); 47 3331, 3707 (1982); 59 2620 (1994) Syn 671 (1978) Z Chem 22 185 (1982) R. C. Larock, "Solvomercuration / Demercuration Reactions in Organic Synthesis," Springer, New York (1986), chpt 2 (review) TL 28 5709 (1987)
$\text{PhHgOH} / \text{H}_2\text{O}$	JOC 47 3331 (1982) ($\text{RC}\equiv\text{CH} \rightarrow \text{RCOCH}_3$ only)
HgO , $\text{BF}_3 \cdot \text{OEt}_2$, $\text{CF}_3\text{CO}_2\text{H} / \text{NaOMe} / \text{H}_2\text{O}$	TL 30 7389 (1989)



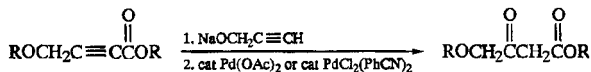
TL 29 6955 (1988)



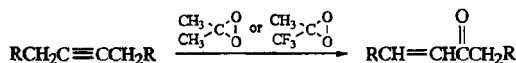
JOC 57 7349 (1992)

 $\text{X} = \text{R}, \text{OR}$

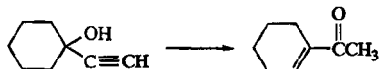
JOC 59 1219 (1994)



TL 34 6309 (1993)



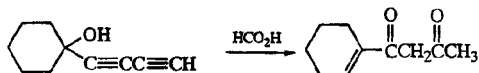
TL 33 7929 (1992)

H⁺

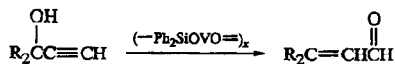
Chem Rev 71 429 (1971) (review)

Nalfion-H

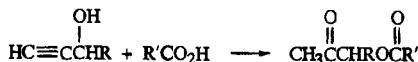
Syn 473 (1981)



TL 23 1051 (1982)



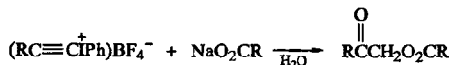
TL 2981 (1976); 23 3193 (1982); 31 7521 (1990)

cat RuCl₂(PMe₃)(cymene)

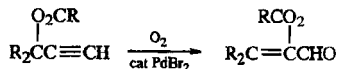
JOC 53 925 (1988)

cat Ru₃(CO)₁₂

JOC 58 7434 (1993)



JOC 54 4038 (1989)

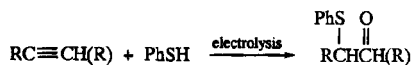


TL 31 4181 (1990)



X = halogen

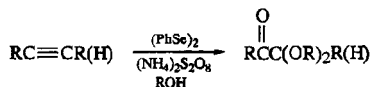
See page 655, Section 4.



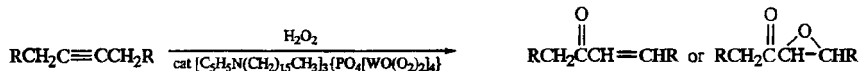
JOC 58 4855 (1993)



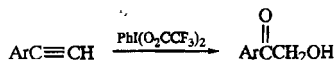
TL 29 2381 (1988)



JOC 56 4529 (1991)



JOC 59 5681 (1994)



Proc Acad Sci USSR, Chem Sec 140 (1979)

 H_5IO_6 , NaHSO_3 ($\text{R} = \text{R}' = \text{Ph}$)

JOC 59 5550 (1994)

 $\text{PhI}(\text{O}_2\text{CCF}_3)_2$ ($\text{R} = \text{R}' = \text{Ar}$)

Proc Acad Sci USSR, Chem Sec 140 (1979)

 $\text{MoO}_5(\text{HMPA})$, cat $\text{Hg}(\text{OAc})_2$

TL 27 5139 (1986)

 H_2O_2 , cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}$
($\text{R} = \text{R}' = \text{Ph}$)

JOC 59 5681 (1994)

 KMnO_4 , H_2O , HOAc , CH_2Cl_2 , phase transfer agent

Syn 462 (1978)

JOC 44 2726 (1979)

JACS 116 8152 (1994)

 KMnO_4 , HOAc , CH_2Cl_2 , phase transfer agent

Syn 462 (1978)

JOC 44 2726 (1979)

 KMnO_4 , NaHCO_3 , MgSO_4 , H_2O , CH_3COCH_3

JOC 44 1574 (1979)

 $\text{Zn}(\text{MnO}_4)_2$, silica gel

JACS 105 7755 (1983)

 H_2O_2 , cat MeReO_3

JOC 60 7728 (1995)

 NaOCl , cat RuO_2

TL 2941 (1971)

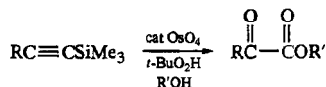
 NaIO_4 , cat RuO_2

TL 2941 (1971); 27 6133 (1986); 34 2677 (1993)

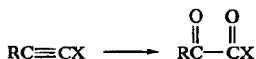
JACS 109 6176 (1987)

 PhIO , cat $\text{RuCl}_2(\text{PPh}_3)_3$

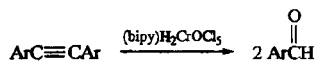
Helv 64 2531 (1981)

 $\text{R}' = \text{H}$ or alkyl

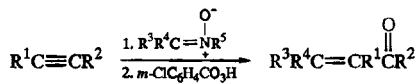
TL 27 1947 (1986)



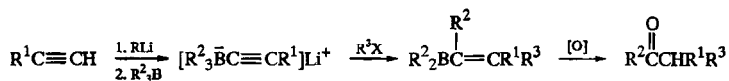
<u>X</u>	<u>Reagent(s)</u>	
OR	KMnO ₄	JOC 60 6221 (1995)
	PhIO, cat RuCl ₂ (PPh ₃) ₃	TL 23 3661 (1982)
NR ₂	PhIO, cat RuCl ₂ (PPh ₃) ₃	TL 23 3661 (1982)



Org Prep Proc Int 14 362 (1982)

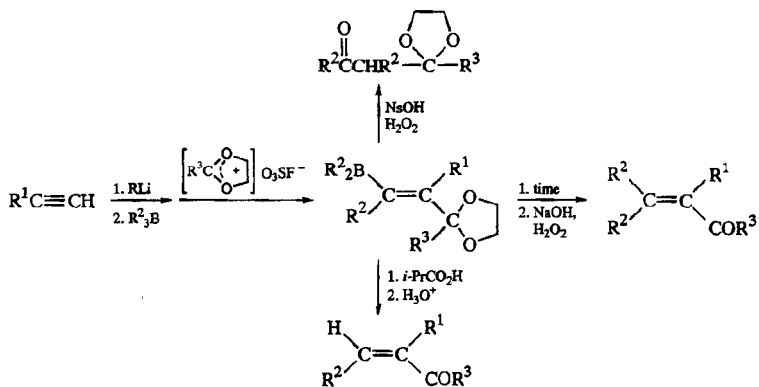


TL 28 913 (1987)

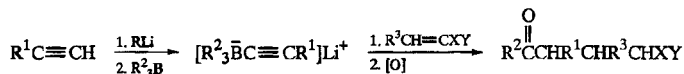


CC 544 (1973)

TL 2741 (1973); 28 1003 (1987)



TL 27 1935 (1986)

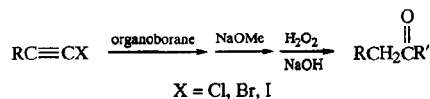
X

H, Me

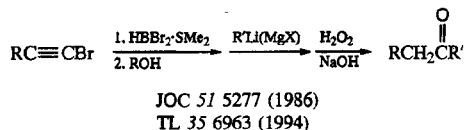
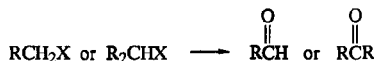
COMe, CO₂EtYNO₂CO₂Et

CC 913 (1977)




TL 22 797 (1981)

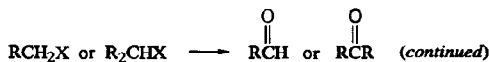
**Organoborane**

$\text{R}'\text{BHR-SMe}_2$	JOC 47 3808 (1982); 51 5270 (1986)
$\text{R}'_2\text{BH}$	JOC 47 754 (1982); 51 5270 (1986)
$(\text{CH}_3)_2\text{CHC}(\text{CH}_3)_2\text{BHR}'$	Syn 193 (1982) JOC 51 5270 (1986) JACS 110 1529 (1988)

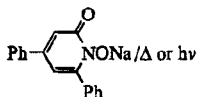
**7. Halides, Nitrates and Sulfonates**

Reagent(s)	Substrate	
O_2 , Al, cat $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, DMF	1° allylic iodide	SL 660 (1990)
O_2 , VOSO_4 or $\text{VO}(\text{acac})_2$, DMF	1° allylic iodide	SL 660 (1990)
DMSO	—	Chem Rev 67 247 (1967) (review)
	$\text{ArCH}_2\text{Cl}(\text{Br})$, Ar_2CHCl	JACS 79 6562 (1957) JOC 24 1792 (1959)
	RCOCH_2Br , RCOCHRBr $\text{BrCH}_2\text{CO}_2\text{Et}$	JACS 79 6562 (1957) Chem Ind 88 (1959)
DMSO, NaHCO_3	RCH_2I ArCH_2Br	JCS 520 (1964) JACS 114 6227 (1992) JOC 58 7598 (1993)
	1° allylic chloride (bromide)	TL 2743 (1972) Syn 608 (1984) SL 119 (1993) JOC 59 3762 (1994)
	RCOCHRBr RCH_2OTs	JOC 29 3495, 3498 (1964) JACS 81 4113 (1959) JOC 57 3173 (1992)
DMSO, Na_2CO_3 , NaI	RCOCHRBr	JOC 40 1990 (1975)
DMSO, $\text{NaOAc} \cdot 3\text{H}_2\text{O}$	$\text{RCOCH}_2\text{ONO}_2$	JACS 88 865 (1966)

DMSO, collidine	ArCH ₂ Br RCH ₂ OTs	JOC 51 1088 (1986) JOC 51 1264 (1986); 57 4374 (1992); 60 2792 (1995) TL 35 6781 (1994)
DMSO, Ag ₂ CO ₃	ArCH ₂ Br	TL 34 3519 (1993)
DMSO, AgClO ₄ , organic amine	1° RBr(I), ArCH ₂ Br	CC 1338 (1970)
DMSO, AgBF ₄ /Et ₃ N	RCH ₂ Br, R ₂ CHBr, 1° allylic chloride (bromide)	TL 917 (1974)
DMSO, AgOTs/Et ₃ N	ArCH ₂ Br	JOC 54 2190 (1989)
AgOTs/DMSO, NaHCO ₃	RCH ₂ Cl(Br, I), ArCH ₂ Br	JACS 81 4113 (1959)
AgNO ₃ /DMSO, NaOAc·3H ₂ O	RCOCH ₂ Br, RCOCHRBr	JACS 88 865 (1966)
DMSO, Me ₃ NO	RCH ₂ Br, ArCH ₂ Br, 1° allylic chloride (bromide)	TL 31 4825 (1990)
Me ₃ NO, Δ	RCH ₂ Br(I), ArCH ₂ Br, R ₂ CHBr	Ber 94 1360 (1961)
NMO	1° allylic iodide	TL 31 4155 (1990)
	1° allylic chloride	BCSJ 59 3287 (1986)
 · LiI·2H ₂ O	1° allylic chloride	BCSJ 59 3287 (1986)
Me ₂ N-  , (DBU)	RCH ₂ Cl(Br), ArCH ₂ Cl(Br), R ₂ CHBr	BCSJ 54 2221 (1981)
(CH ₂) ₆ N ₄ , H ₂ O, H ⁺	ArCH ₂ Cl(Br)	Org Syn 30 67 (1950) Org Rxs 8 197 (1954) (review) Syn 161 (1979) (review) JACS 106 3297 (1984); 112 7599 (1990)
<i>i</i> -PrNO ₂ , NaOEt	ArCH ₂ Br	JOC 59 3821 (1994)
NaSPh/NCS/Na ₂ CO ₃ or HgCl ₂ -CdCO ₃	RCH ₂ Br, ArCH ₂ Br	Syn Commun 6 575 (1976)
KO ₂ SePh, 18-crown-6	ArCH ₂ Cl	TL 28 2933 (1987)
KO ₂ SePh, K ₂ HPO ₄	ArCH ₂ Cl(Br)	Syn 747 (1984)
Me ₂ SeO, K ₂ HPO ₄	ArCH ₂ Cl(Br)	Syn 747 (1984)
NaN(SOPh)Cy/Δ/H ₂ O	ArCH ₂ Cl, 1° allylic bromide	JOC 46 4617 (1981)
<i>p</i> -AcOC ₆ H ₄ N(Tf)Na/NaOEt/ HCl	RCH ₂ I, ArCH ₂ Br	JOC 44 1835 (1979)
PhNHTf, K ₂ CO ₃ /HCl	RCOCHRBr, RO ₂ CCHRBr	JOC 44 1835 (1979)

ReagentsSubstrateIF₅/H₂ORCH₂I, R₂CHI, ArCH₂Br,
ArCHRBBr

Syn 419 (1977)

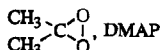
(n-Bu₄N)₂Cr₂O₇R₂CHBr, ArCH₂Cl(Br),
1° allylic bromideChem Ind 213 (1979)
JOC 51 3347 (1986)
TL 31 3883 (1990)ArCH₂Cl(Br), ArCHRBBr

JCS Perkin I 2493 (1979)

XYReagent(s)

OR

Br



TL 36 7735 (1995)

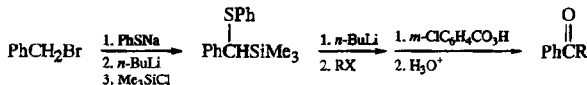
p-NO₂C₆H₄SO₃Et₃N

JOC 55 2820 (1990)

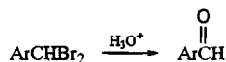
NR₂*p*-NO₂C₆H₄SO₃

DBU

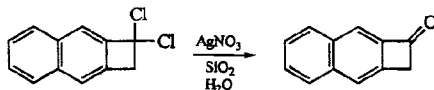
JOC 56 6435 (1991)



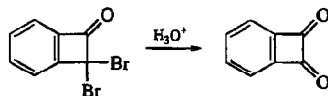
TL 21 4759 (1980)



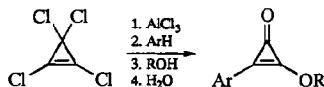
JACS 112 7599 (1994); 114 6227 (1992)



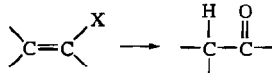
TL 32 7097 (1991)



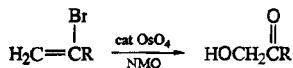
JOC 54 1435 (1989)



JOC 59 4319 (1994)

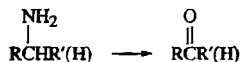


<u>X</u>	<u>Reagent(s)</u>	
F	Hg(OAc) ₂ , CF ₃ CO ₂ H/NaHCO ₃	CL 651, 935 (1980)
Cl	H ₂ SO ₄	Coll Czech Chem Commun 12 93, 101, 129 (1947) TL 29 1751 (1988) Org Syn Coll Vol 6 142 (1988) BSCF 1941 (1976) TL 3489 (1979)
	Hg(OAc) ₂ , HCO ₂ H	TL 1943 (1978) TL 1943 (1978)
	Hg(OAc) ₂ , HOAc, BF ₃ ·OEt ₂	TL 1943 (1978)
	Hg(OAc) ₂ , CF ₃ CO ₂ H	TL 3489 (1979); 22 425 (1981)
	Hg(O ₂ CCF ₃) ₂ , CH ₃ NO ₂	Helv 63 1383 (1980) JOC 55 5625 (1990); 60 594 (1995)
Br	Hg(O ₂ CCF ₃) ₂ , CH ₃ NO ₂	JACS 111 5496 (1989)


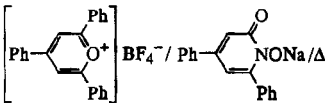
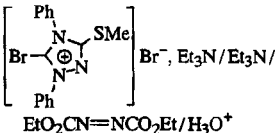


TL 34 4485 (1993)

8. Amines



Aldehydes only

CuO ₂ H	TL 31 3891 (1990)
 /LDA/H ⁺	JOC 46 1937 (1981)
	JCS Perkin I 2500 (1979)
	TL 2131 (1978)
cyclohexanone / ArSOCl / Δ / H ₂ O	JOC 46 4617 (1981)

Ketones onlyNCS/NaOMe/H₂SO₄, H₂O

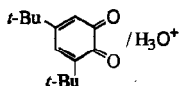
Coll Czech Chem Commun 24 2975 (1959)

NBS/base/H₃O⁺

JACS 90 3245 (1968)

(PhIO)_n

TL 29 6913 (1988)

Ph₃P, *i*-PrO₂CN=NCO₂-*i*-PrTL 29 4661 (1988) [PhCH(NH₂)CO₂Me]

JACS 91 1429 (1969); 112 760 (1990)

TL 29 851 (1988)

JOC 53 5994 (1988)

Aldehydes and ketonescat Na₅PMo₂V₂O₄₀-C

JOC 56 5707 (1991)

KMnO₄, *t*-BuOH, H₂O (R₂CO > RCHO)

JOC 32 3129 (1967)

t-BuOCl, NaHCO₃/NaOEt/H₂SO₄, H₂O

JACS 76 5554 (1954)

IF₅/H₂O

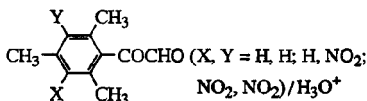
Syn 419 (1977)

Ag(O₂CC₃H₄N)₂

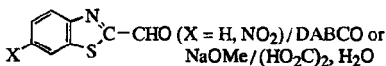
JCS 4962 (1965)

AgNO₃, Na₂S₂O₈, NaOH

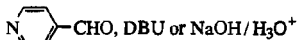
JCS C 1384, 1388 (1966)



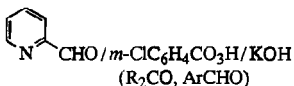
JACS 91 1429 (1969)



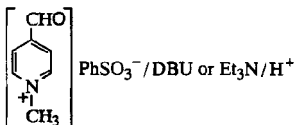
JCS Perkin I 1652 (1972)



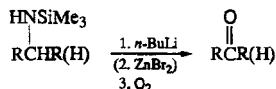
Syn 756 (1982)



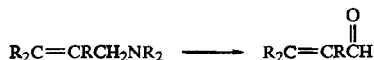
JACS 97 6900 (1975)



JACS 104 4446 (1982)



TL 29 6701 (1988)



air, cat I₂, hv, EtOH

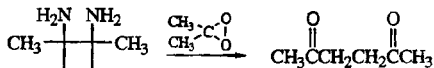
JOC 55 3679 (1990)

H₂O₂/Ac₂O

CL 1987 (1982)

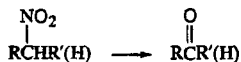


Org Rxs 39 85 (1990) (review)



TL 36 1803 (1995)

9. Nitro Compounds



Review: Chimia 33 1 (1979)

Aldehydes only

NaO-*t*-Bu/KMnO₄

JOC 46 1037 (1981)

SnCl₂·2H₂O, PhSH, Et₃N/SnCl₂·2H₂O, tartaric acid, NaHCO₃, NaHSO₃

TL 31 7499 (1990)

Ketones only

KH/HCl

JACS 113 5917 (1991)

KMnO₄, silica gel

CC 635 (1982)

NaNO₂, *n*-C₃H₇ONO

JOC 38 1418 (1973)

Ber 108 1946 (1975)

VCl₂, HCl, H₂O

TL 2533 (1976)

CAN, Et₃N, H₂O

TL 23 3521 (1982)

R₃SiCl, DBU/*m*-ClC₆H₄CO₂H

TL 28 5361 (1987)

KO-*t*-Bu/*t*-BuO₂H, VO(acac)₂ or Mo(CO)₆

TL 331 (1977)

JOC 55 1349 (1990)

LDA/MoO₅·py·HMPA

TL 22 5235 (1981)

Triton B/O₃

TL 28 2883 (1987)

Aldehydes and ketones

OH⁻/H⁺ (Nef reaction)

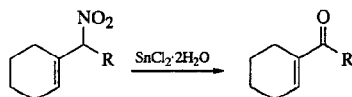
Chem Rev 55 137 (1955) (review)

TL 1331 (1972); 3215 (1974)

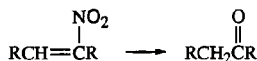
JACS 99 3862 (1977); 108 1039 (1986)

Org Rxs 38 655 (1990) (review)

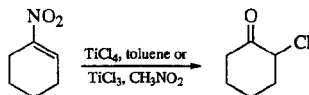
KOH or NaH- <i>t</i> -BuOH / KMnO ₄	Ber 69 1789 (1936); 38 3440 (1973) JOC 27 3699 (1962); 47 4534 (1982) TL 569 (1973)
KOH / KMnO ₄ , H ₂ O, MgSO ₄	JOC 50 4971 (1985); 54 4034 (1989)
NaOH, NaClO ₂ , (<i>n</i> -Bu ₄ N)HSO ₄	TL 30 5329 (1989)
NaOH or NaOCH ₃ / O ₃	JOC 39 259 (1974) Helv 61 984 (1978) Org Syn Coll Vol 6 648 (1988)
NaOCH ₃ / ¹ O ₂	JOC 43 1271 (1978)
NaOCH ₃ / TiCl ₃	JOC 51 4368 (1986); 53 4676 (1988)
NaOCH ₃ -silica gel	Org Prep Proc Int 10 9 (1978)
NaOCH ₃ / silica gel	JACS 99 3861 (1977)
Et ₃ N / CAN	Syn 44 (1980)
Et ₃ N / (<i>n</i> -C ₁₆ H ₃₃ NMe ₃)MnO ₄	Syn Commun 17 195 (1987)
H ₂ O ₂ , K ₂ CO ₃	Syn 662 (1980)
TiCl ₃ , NH ₄ OAc	JACS 93 5309 (1971) JOC 38 4367 (1973)
CrCl ₂ , CH ₃ OH, HCl	Syn 792 (1977)



TL 34 869 (1993)

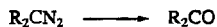


LiHB(<i>sec</i> -Bu) ₃ / H ₂ SO ₄ , H ₂ O	Syn 654 (1985)
<i>n</i> -Bu ₃ SnH / O ₃ or <i>m</i> -ClC ₆ H ₄ CO ₃ H	TL 28 5365 (1987)
CrCl ₂ , HCl, H ₂ O	TL 26 3777 (1985)
Raney Ni, NaH ₂ PO ₂ ·H ₂ O	TL 24 417 (1983)
Raney Ni, (Et ₃ NH)H ₂ PO ₂ ·1.5H ₂ O	JOC 54 949 (1989)
electrolysis	CL 607 (1983)



JOC 60 8320 (1995)

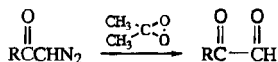
10. Diazo Compounds



JOC 36 3774 (1971)

PhCO₃H

TL 35 5625 (1994); 36 3719 (1995)



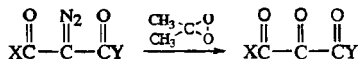
TL 32 6215 (1991)

*m*-ClC₆H₄CO₃H

TL 35 2929 (1994)



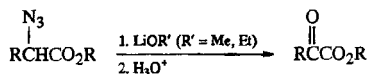
TL 35 5625 (1994)



X, Y = R, R; R, OR; OR, OR

Syn Commun 24 695 (1994)

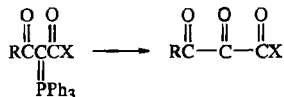
11. Azides



JOC 45 4952 (1980)

SL 962 (1992)

12. Phosphorus Ylids

X = OR, NR₂¹O₂

JOC 54 2785 (1989)

JACS 111 371 (1989)

O₃

JOC 54 2785 (1989)

JACS 111 371 (1989)

TL 30 869, 873 (1989)

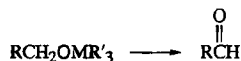
oxone

JOC 58 4785 (1993)



JOC 60 8231 (1995)

13. Ethers

MReagent(s)

Si

NBS, hv
NBS, cat AIBN
DDQ, hv

JOC 43 371 (1978) (R = aryl)
SL 345 (1990) (R = aryl)
TL 32 3993 (1991)
(R = aryl, vinylic)

(NO)BF₄

Syn 609 (1976) (R = aryl)

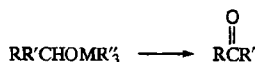
Sn

NBS

JACS 98 1629 (1976)

(NO)BF₄

(R = aryl, vinylic)
Syn 609 (1976) (R = aryl)

MReagent(s)

Si

NBS, py, hv
NBS, cat AIBN
DDQ, hv

JOC 43 371 (1978)
SL 345 (1990) (R = aryl)
TL 32 3993 (1991)
(R = aryl, vinylic)

(NO)BF₄

Syn 609 (1976)

NaBrO₃, cat CAN, H₂O

Syn 897 (1980)

t-BuO₂H, cat (Ph₃SiO)₂CrO₂

SL 497 (1991)

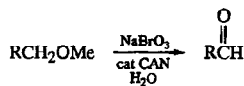
Sn

NBS

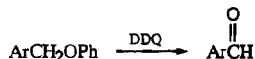
JACS 98 1629 (1976)

(NO)BF₄

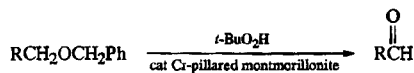
Syn 609 (1976)



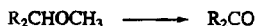
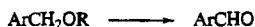
Syn 897 (1980)



JOC 55 1555 (1990)



JOC 57 5841 (1992)



NaBrO₃, cat CAN, H₂O (Me, Et and
PhCH₂ ethers)

Syn 897 (1980)

IF₅ / H₂O

Syn 419 (1977)

UF₆/H₂O

JACS 98 6717 (1976); 100 5396 (1978)

(NO₂)BF₄

JOC 42 3097 (1977)

NO₂, SiO₂

CC 1607 (1990)

Cu(NO₃)₂-SiO₂

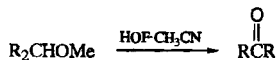
JOC 54 3001 (1989); 55 5606 (1990)

Zn(NO₃)₂-SiO₂

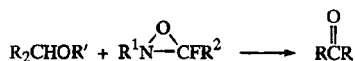
JOC 54 3001 (1989); 55 5606 (1990)



TL 33 7399 (1992)

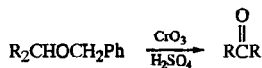


JOC 60 8267 (1995)

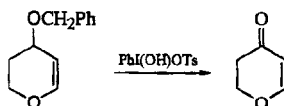


R' = 1° alkyl, PhCH₂; R¹, R² = n-C₄F₉, n-C₃F₇; n-C₆F₁₃, n-C₃F₁₁

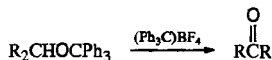
JOC 60 2314 (1995)



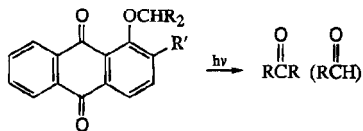
JOC 46 1492 (1981)



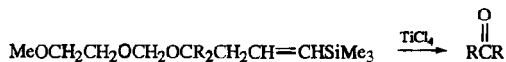
SL 289 (1993)



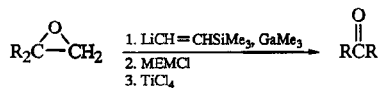
JACS 98 7882 (1976)



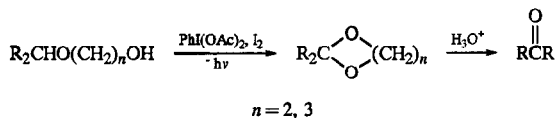
JOC 60 6852 (1995)



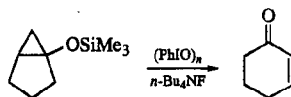
TL 35 7977 (1994)



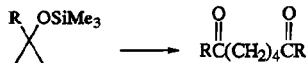
TL 35 7977 (1994)



TL 29 2215 (1988)



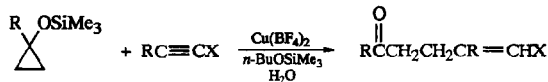
TL 31 197 (1990)

 $\text{Cu}(\text{BF}_4)_4$

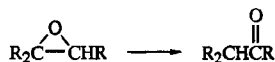
JACS 105 7192 (1983); 115 12330 (1993)

 AgBF_4

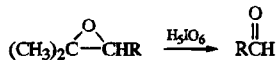
JACS 105 7192 (1983)

 $\text{X} = \text{CO}_2\text{R}, \text{COR}, \text{SO}_2\text{R}$

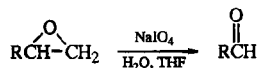
JACS 115 12330 (1993)



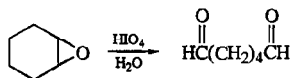
See page 1277, Section 2.



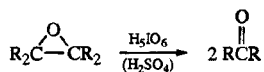
JOC 51 5447 (1986); 57 7226 (1992)



CC 1434 (1987)

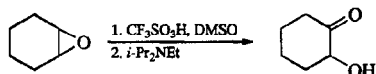


TL 4599 (1973)



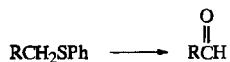
JACS 105 4113 (1983); 107 686 (1985)

JOC 54 3324, 3329 (1989)



TL 29 2163 (1988)

14. Sulfides

NCS/CuO, CuCl₂, H₂O

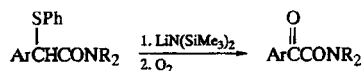
JOC 41 3261 (1976); 55 555 (1990)

NCS/HgCl₂, H₂O

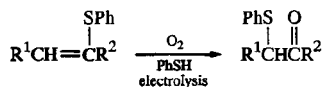
TL 29 1461 (1988)

SO₂Cl₂/H₂O, silica

JOC 48 3571 (1983)

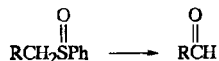


JACS 112 9601 (1990)



JOC 58 4855 (1993)

15. Sulfoxides

Ac₂O, NaOAc/K₂CO₃, MeOH

JACS 114 10232 (1992)

(CF₃CO)₂O, py/NaHCO₃

JOC 59 5532 (1994)

(CF₃CO)₂O, 2,4,6-Me₃C₃H₂N/CuCl₂, H₂O

JOC 55 4216 (1990)

16. Sulfones

LDA / MoO₅·py·HMPA

TL 21 3339 (1980); 27 5951 (1986); 29 451 (1988)
 JACS 104 6115 (1982); 107 1034 (1985) (enal); 111
 1826 (1989)
 JOC 51 5311 (1986); 59 885 (1994)

n-BuLi / (Me₃SiO)₂

JOC 48 4432 (1983)

n-BuLi / ClB(OMe)₂ / *m*-ClC₆H₄CO₂H

TL 26 2333 (1985)

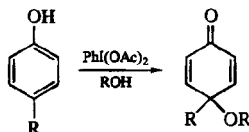
n-BuLi / CCl₄ / AgClO₄, CF₃CO₂H

BCSJ 53 3027 (1980) (aryl ketones only)

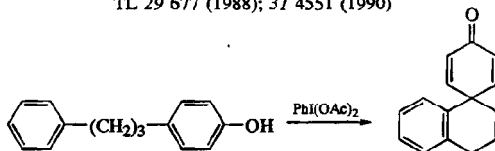
KO-*t*-Bu / *p*-ClC₆H₄CH(OMe)NSO₂C₆H₄Cl-*p*
 (2-sulfonyl-1-alkanones to 1,2-alkanediones)

JOC 57 3740 (1992)

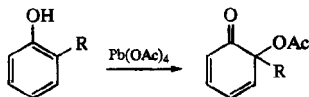
17. Phenols



TL 29 677 (1988); 31 4551 (1990)

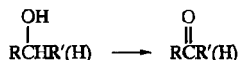


TL 31 1351 (1990)



Monatsh 81 811, 1055 (1950)
 TL 24 147 (1983); 32 4439 (1991)
 Can J Chem 66 1 (1988)
 CC 739 (1990)

18. Alcohols



Reviews:

"activated" DMSO reagents

Chem Rev 67 247 (1967)

Tetr 34 1651 (1978)

Cr(VI)

other methods

Syn 165 (1981); 857 (1990)

Org Rxns 39 297 (1990)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 2.8, p 281

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 2.7, p 251

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 2.9, p 305

Aldehydes only

horse liver alcohol dehydrogenase

TL 29 5769 (1988)

benzoquinone ($\text{ArCH}=\text{CHCH}_2\text{OH}$)

TL 31 4497 (1990)

DMSO, air, Δ (allylic, benzylic)

JACS 86 298 (1964)

DMSO, py- SO_3 , *i*-Pr₂NEt

TL 28 1603 (1987)

cat SeO_2 - SiO_2 , *t*-BuO₂H, (allylic)

SL 425 (1992)

C₆F₅SeO₂H

TL 35 5149 (1994)

cat (ArSe)₂, *t*-BuO₂H

TL 2801 (1979)

 $[\text{M}(\text{H}_2\text{TeO}_6)_2]^{5-}$ (M = Ag, Cu; benzylic)

JOC 59 858 (1994)

NaOCl, KBr, cat TEMPO

JOC 52 2559 (1987)

TL 33 5029 (1992)

NBS, *n*-Bu₄NI, hv (benzylic)

JOC 60 6602 (1995)

NIS, hv (benzylic)

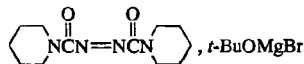
JOC 48 3126 (1983)

 $[\text{ClCH}_2\text{N}^+\text{C}_6\text{H}_4\text{N}^+\text{F}](\text{BF}_4)_2$ (benzylic)

SL 831 (1994)

OTs⁻, Et₃N/hexamine (benzylic)

CL 369 (1978)



JACS 106 7970 (1984)

TL 28 527 (1987)

n-PrMgBr/*t*-BuOMgBr, *m*-ClC₆H₄CO₂H

BCSJ 50 2773 (1977)

n-PrMgBr/*t*-BuOMgBr, NCS

BCSJ 50 2773 (1977)

Pb(OAc)₄, Mn(OAc)₂

TL 27 2287 (1986)

CrO₃-graphite

Can J Chem 50 3058 (1972)

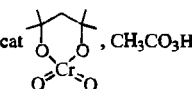
(DMAP)HCrO₃Cl (allylic, benzylic)

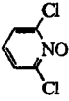
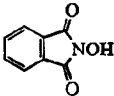
JOC 47 1787 (1982)

MnO₂, bentonite, microwave or ultrasound
(allylic, benzylic)


TL 34 5293 (1993)

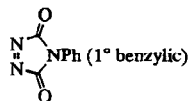
BaMnO ₄ -Celite (allylic)	JOC 57 5058 (1992)
K ₂ FeO ₄ (benzylic)	CL 1397 (1978)
RuCl ₂ (PPh ₃) ₃	TL 22 1605 (1981) JACS 111 7525 (1989)
cat RuCl ₂ (PPh ₃) ₃ , (Me ₃ SiO) ₂	TL 24 2185 (1983)
cat RuCl ₂ (PPh ₃) ₃ , PhI(OAc) ₂	TL 22 2361 (1981)
cat RuCl ₃ , NaIO ₄ , H ₂ O, CH ₃ CN	JOC 52 4592 (1987)
cat CuCl, O ₂ , cat TEMPO (allylic, benzylic)	JACS 106 3374 (1984)
CuCl ₂ , O ₂ , cat TEMPO (alkyl, allylic, benzylic)	JACS 106 3374 (1984)
Ketones only	
O ₃	JOC 41 889 (1976)
<i>m</i> -ClC ₆ H ₄ CO ₂ H, 10% HCl	TL 4115 (1975)
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \\ \diagdown \\ \text{CH}_3 \end{array}$	TL 35 8477, 8751 (1994)
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}_f\text{N}-\text{CFR}_f \end{array}$	TL 33 7245 (1992)
DDQ (allylic or benzylic)	JOC 50 5897 (1985); 58 361 (1993)
DDQ, HIO ₄ (allylic)	Syn 848 (1978)
DMSO, <i>i</i> -PrN=C=N- <i>i</i> -Pr, cat Cl ₂ CHCO ₂ H	JACS 107 3285 (1985)
(Ph ₃ C)BF ₄	TL 2771 (1978)
tetrazolium salt, KOH, EtOH (α -hydroxy ketone)	TL 28 4323 (1987)
<i>Bacillus stearothermophilus</i> (enantioselective)	TL 36 441 (1995)
cat SeO ₂ , <i>t</i> -BuO ₂ H (allylic)	TL 28 3831 (1987)
cat C ₆ F ₅ SeO ₂ H, <i>t</i> -BuO ₂ H	TL 35 5149 (1994)
NaOCl, HOAc	JOC 45 2030 (1980); 52 2602 (1987) TL 23 4647 (1982)
Ca(OCi) ₂ , HOAc, CH ₃ CN	TL 23 35 (1982)
Br ₂ (quinuclidine) ₂ , (C ₅ H ₅ NH) ₂ O ₂ CCF ₃	JOC 57 1600 (1992)
PhICl ₂ , py	TL 3635 (1973)
(<i>t</i> -BuO) ₃ Al or Me ₃ Al, <i>t</i> -BuO ₂ H	TL 21 1657 (1980)
Al(O- <i>i</i> -Pr) ₃ , CH ₃ COCH ₃	JOC 53 3912 (1988)
cat VO(acac) ₂ , <i>t</i> -BuO ₂ H	TL 24 5009 (1983)
CrO ₃ , HOAc	JACS 75 422 (1953)
cat CrO ₃ , <i>t</i> -BuO ₂ H, H ₂ O (benzylic)	TL 28 2133 (1987)
Na ₂ Cr ₂ O ₇ ·2H ₂ O-H ₂ SO ₄ -silica gel	Tetr 35 1789 (1979)

$\text{K}_2\text{Cr}_2\text{O}_7$, H_2SO_4 , ether (alkyl, allylic)	JACS 83 2952 (1961) JCS C 1972 (1966) JOC 36 387 (1971) Org Syn Coll Vol 8 386 (1993)
cat  , $\text{CH}_3\text{CO}_3\text{H}$	TL 26 5855 (1985)
PCC, ultrasound	TL 36 1845 (1995)
PDC, HOAc, EtOAc (allylic only)	JOC 51 5472 (1986)
PDC, $(\text{C}_5\text{H}_5\text{NH})\text{O}_2\text{CCF}_3$	JACS 109 4690 (1987)
cat $\text{Mo}(\text{CO})_6$, $t\text{-BuO}_2\text{H}$, cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]\text{Cl}$, MgSO_4	Syn 59 (1986)
cat $(\text{PhCH}_2\text{NMe}_3)\text{OMoBr}_4$, $t\text{-BuO}_2\text{H}$	TL 25 4417 (1984)
cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PMo}_{12}\text{O}_{40}$, $t\text{-BuO}_2\text{H}$	Syn Commun 16 537 (1986)
cat $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, H_2O_2 , $n\text{-Bu}_4\text{NCl}$, K_2CO_3	TL 25 173 (1984) JACS 114 7375 (1992)
cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PW}_{12}\text{O}_{40}$, H_2O_2	JOC 53 3587 (1988)
MnO_2 , cat $[\text{RuCl}_2(\text{cymene})]_2$, cat 2,6-di- t -butylbenzoquinone, cat K_2CO_3	JOC 59 1196 (1994)
$\text{NaMnO}_4 \cdot \text{H}_2\text{O}$ (solid)	TL 22 1655 (1981)
KMnO_4 , ion exchange resin	JOC 54 4993 (1989)
KMnO_4 , $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$	JOC 44 3446 (1979)
$\text{Cu}(\text{MnO}_4)_2 \cdot 8\text{H}_2\text{O}$	JOC 47 2790 (1982)
cat MeReO_3 , H_2O_2	TL 36 6415 (1995)
cat $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $t\text{-BuO}_2\text{H}$, cat picolinic acid, py, HOAc	TL 35 4681 (1994)
cat RuO_2 , NaIO_4	JOC 50 2759 (1985)
cat RuO_2 , NaIO_4 , cat $(\text{PhCH}_2\text{NEt}_3)\text{Cl}$	JOC 52 1149 (1987)
cat $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$, electrolysis	JOC 51 151 (1986)
cat $\text{RuO}_2 \cdot x\text{H}_2\text{O}$, NaBrO_3	JOC 53 1103 (1988)
cat K_2RuO_4 , K_2SO_5	CC 58 (1979)
$n\text{-Pr}_4\text{N}(\text{RuO}_4)$	JACS 112 2003 (1990)
cat $\text{R}_4\text{N}(\text{RuO}_4)$ ($\text{R} = n\text{-Pr}$, $n\text{-Bu}$), NMO	CC 1625 (1987) JOC 59 1907 (1994)
$\text{RuCl}_2(\text{PPh}_3)_3$, K_2CO_3	TL 31 1735 (1990)
cat $\text{RuCl}_2(\text{PPh}_3)_3$, PhIO	TL 22 2361 (1981)
cat $\text{RuCl}_2(\text{PPh}_3)_3$, 4- $\text{PhCO}_2\text{-TEMPO}$, O_2	TL 36 3223 (1995)

cat RuCl_3 , NaOCl	CC 1420 (1970) JOC 48 1366 (1983)
cat $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $\text{CH}_3\text{CO}_3\text{H}$	SL 733 (1995)
cat $\text{RuCl}_3\text{-Co}(\text{OAc})_2$, O_2 , CH_3CHO	JOC 58 7318 (1993)
cat Ru porphyrin, 	JACS 114 10660 (1992)
cat OsO_4 , $t\text{-BuO}_2\text{H}$, Et_4NOH (allylic)	TL 35 7221 (1994)
cat $\text{Co}(\text{acac})_3$, O_2 , cat 	TL 36 6923 (1995)
cat Co Schiff base, O_2 , Me_2CHCHO	TL 35 4847 (1994)
cat $\text{IrH}_5(i\text{-Pr}_3\text{P})_2$	TL 28 3115 (1987)
Raney Ni (1-octene)	JOC 51 5482 (1986); 53 3158 (1988)
$\text{Pd}(\text{OAc})_2$, H_2O , DMF (allylic)	SL 861 (1993)
cat PdCl_2 , K_2CO_3 , CCl_4 , Δ	CL 1171 (1981)
PdCl_2 , O_2 , NaOAc	CC 157 (1977)
cat $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , PhBr , DMF	TL 1401 (1979) JOC 48 1286 (1983)
$\text{Cu}(\text{OAc})_2$, HOAc	Org Syn Coll Vol 4 838 (1963) JACS 117 163 (1995)
CAN or $\text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{SO}_4$, NaBrO_3	TL 23 539 (1982) JOC 50 2759 (1985)
cat $\text{Yb}(\text{O-}i\text{-Pr})_3$, 2-butanone, molecular sieves	TL 32 2355 (1991)
electrolysis, KI, H_2O	TL 165 (1979)
electrolysis, poly-4-vinylpyridine $\cdot \text{HBr}$	JOC 45 5269 (1980)
electrolysis, $n\text{-C}_8\text{H}_{17}\text{SCH}_3$, Et_4NBr	TL 21 1867 (1980)
electrolysis, NiOOH	Tetr 38 3299 (1982)

Aldehydes and ketones

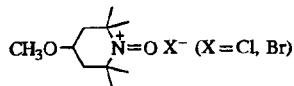
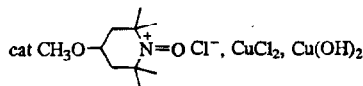
$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$,  $\text{NH}\cdot\text{HCl}$ (1° benzylic)	JOC 40 1860 (1975)
CH_3COCOCl , py/hv	JOC 41 3030 (1976)
DDQ (1° or 2° benzylic)	JOC 45 1596 (1980)
5-deazaflavin, KOH (1° benzylic)	CC 825 (1977)
$\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$, $\text{EtO}_2\text{CCH}_2\text{NO}_2$, PPh_3	TL 2295 (1981)



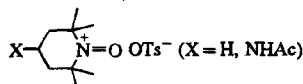
CC 744 (1966)

(NO)BF₄ (1° or 2° benzylic)

Syn 609 (1976)

JOC 50 1332 (1985); 55 1490 (1990)
TL 29 5671 (1988)

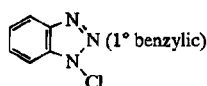
JOC 55 1490 (1990)



JOC 56 6110 (1991)

trichloromelamine

JOC 58 5003 (1993)



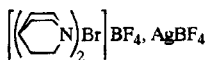
JCS C 1474 (1969)

NBA, NBS or NCS (1° benzylic)

Chem Rev 63 21 (1963) (review)

NIS, *n*-Bu₄NI

Syn 394 (1981)



JOC 51 5454 (1986)

(p-Tol₃BiO)_n

TL 35 8197 (1994)

(Ph₃BiCl)₂O

CC 1099 (1978)

DMSO, Ac₂O

JOC 30 1107 (1965)

JACS 87 4214 (1965); 89 2416 (1967); 109 7477
(1987) (2-hydroxy-1-alkanone to 1,2-alkanedione)DMSO, (PhCO)₂O

JACS 89 2416 (1967)

DMSO, (CF₃CO)₂O/Et₃N

JOC 41 957, 3329 (1976); 52 4851 (1987)

(1,2-alkanediols to 1,2-alkanediones)

Syn 297 (1978)

DMSO, (COCl)₂/Et₃N (Swern)JOC 43 2480 (1978); 44 4148 (1979); 50 2198
(1985); 51 5282 (1986); 52 5700 (1987); 58 3912
(1993)

Tetr 34 1651 (1978)

Syn 165 (review), 567 (3-hydroxy-1-alkanones,
3-hydroxyalkanoate esters) (1981)

Org Syn 64 164 (1985)

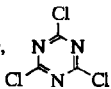
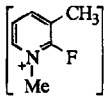

JACS 108 1035, 4603 (1986); 109 3353 (1987); 110
6785 (1988)

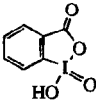
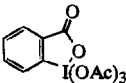
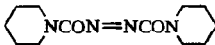
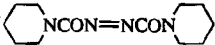
TL 29 49 (1988)

Org Syn Coll Vol 7 258 (1990)

DMSO/COCl₂/Et₃N

JCS 1855 (1964)

DMSO, $\text{Cl}_3\text{COCOC}_1/\text{Et}_3\text{N}$	TL 29 6619 (1988)
DMSO, $\text{Cl}_3\text{COCO}_2\text{CCl}_3/\text{Et}_3\text{N}$	JOC 56 5948 (1991)
DMSO, DCC, H^+ (Pfitzner-Moffatt)	JACS 85 3027 (1963); 87 5661, 5670 (1965); 88 1762 (1966) Org Syn 47 25 (1967) Chem Rev 67 247 (1967) (review)
DMSO, polymer- $\text{N}=\text{C}=\text{N}-i\text{-Pr}$, H_3PO_4	TL 3285 (1972) Org Syn Coll Vol 6 218 (1988)
DMSO, polyphosphoric acid	JACS 89 2416 (1967)
DMSO, P_2O_5	JACS 87 4214, 4651 (1965); 89 2416 (1967)
DMSO, $\text{PhOPOCl}_2/\text{Et}_3\text{N}$	TL 29 3167 (1988) JOC 59 7704 (1994)
DMSO, $\text{py}\cdot\text{SO}_3$, Et_3N	Chem Pharm Bull 30 1921 (1982) JOC 52 1252 (1987)
DMSO, $\text{py}\cdot\text{SO}_3/\text{Et}_3\text{N}$	JACS 89 5505 (1967)
DMSO, $\text{SOCl}_2/\text{Et}_3\text{N}$	Tetr 34 1651 (1978)
DMSO, $\text{PhSO}_2\text{Cl}/\text{Et}_3\text{N}$	JOC 39 1977 (1974)
DMSO, $\text{TsCl}/\text{Et}_3\text{N}$	JOC 39 1977 (1974)
DMSO, $\text{ClSO}_2\text{NCO}/\text{Et}_3\text{N}$ (1° allylic or benzylic)	Syn 141 (1980)
DMSO, $(\text{MeSO}_2)_2\text{O}/\text{Et}_3\text{N}$	JOC 39 1977 (1974)
DMSO, Ts_2O	JOC 39 1977 (1974)
DMSO, $\text{Cl}_2/\text{Et}_3\text{N}$	TL 919 (1973)
DMSO,  $/\text{Et}_3\text{N}$	JOC 39 1977 (1974)
DMSO,  OTs^- , Et_3N	CL 369 (1978)
 SO_2 , Ac_2O	JACS 89 2416 (1967)
Me_2S , $\text{NCS}/\text{Et}_3\text{N}$	JACS 94 7586 (1972); 112 8465 (1990) JOC 38 1233 (1973); 57 3354 (1992) Org Syn Coll Vol 6 220 (1988)
Me_2S , $\text{Cl}_2/\text{Et}_3\text{N}$	JACS 94 7586 (1972) JOC 51 5282 (1986)
PhSMc , $\text{NCS}/i\text{-Pr}_2\text{NEt}$	JOC 52 4505 (1987)


PhSeMe, Cl ₂ /Et ₃ N	JOC 38 1233 (1973)
Me ₂ SeO, molecular sieves	Syn 747 (1984)
(PhSeO) ₂ O (1° allylic or benzylic, α-hydroxy lactone)	CC 952 (1978) TL 29 3205 (1988)
(ArSe) ₂ , <i>t</i> -BuO ₂ H	JOC 47 837 (1982)
Cl ₂ , py	TL 3059 (1974)
Cl ₂ or Br ₂ , HMPA (1° benzylic)	Syn 811 (1976)
(<i>n</i> -Bu ₃ Sn) ₂ O/Br ₂ (1° benzylic)	TL 4597 (1976)
Et ₃ SnOMe/Et ₃ SnOMe, Br ₂ (2° alkyl, 1° allylic, 1° or 2° benzylic)	CL 145 (1975)
NaOCl (phase transfer) (1° benzylic)	TL 1641 (1976)
NaOCl, NaBr, cat TEMPO	TL 33 5029 (1992) Org Syn Coll Vol 8 367 (1993)
NaOCl, cat 4-MeO-TEMPO, KBr, NaHCO ₃	JOC 52 2559 (1987)
Ca(OCl) ₂ (1° benzylic)	TL 35 (1982)
Ca(OCl) ₂ , cat 4-PhCO ₂ -TEMPO, NaHCO ₃	JOC 55 462 (1990)
NaBrO ₂ ·3H ₂ O, cat 4-PhCO ₂ -TEMPO, NaHCO ₃	JOC 55 462 (1990)
	TL 35 8019 (1994) JOC 60 7272 (1995)
 (Dess-Martin periodinane)	JOC 48 4155 (1983); 54 661 (1989); 55 5186 (1990); 59 7549, 7825, 7833 (1994) TL 28 2921, 4259 (trifluoromethyl ketones) (1987); 29 1251, 3433 (α-hydroxy esters) (1988); 34 5587 (1993) JACS 111 4852 (1989); 112 7001 (1990); 113 7277 (1991); 115 7152 (1993)
EtMgBr/PhCHO (1° or 2° allylic, 2° alkyl)	TL 28 769 (1987)
<i>n</i> -PrMgBr/ <i>t</i> -BuOMgBr, 	BCSJ 50 2773 (1977) JACS 106 7970 (1984) JOC 57 3359 (1992)
MeMgI/ 	TL 32 4631 (1991)
<i>n</i> -PrMgBr/ <i>t</i> -BuOMgBr, PhI(OAc) ₂	BCSJ 50 2773 (1977)
Al(<i>O-t</i> -Bu) ₃ , CH ₃ COCH ₃ (Oppenauer)	Org Rxs 6 207 (1951) (review)
Pb(OAc) ₄ , py	TL 3071 (1964); 4427 (1967)

- hv, platinised TiO₂ (1° alkyl or allylic, 2° benzylic) TL 25 3363 (1984)
- cat Cp₂ZrH₂, RCOR (1° or 2° alkyl, allylic, benzylic) JOC 51 240 (1986); 52 4855 (1987)
- cat Cp₂Zr(O-*i*-Pr)₂, PhCHO or PhCOPh JOC 52 4855 (1987)
- cat chromia-pillared montmorillonite, *t*-BuO₂H TL 31 5785 (1990)
- CrO₃-polymer JACS 98 6737 (1976)
- CrO₃, HMPA (2° benzylic) Syn 394 (1976)
- CrO₃, Celite, Et₂O, CH₂Cl₂ Syn 815 (1979)
- CrO₃-H₂O-SiO₂ Syn 534 (1978)
- CrO₃, cat *n*-Bu₄NX (X = F, Cl, Br, HSO₄, O₂CCF₃) TL 21 4653 (1980)
- CrO₃·2py (Collins) JACS 75 422 (1953); 111 6648 (1989)
 JOC 26 4814 (1961); 35 4000 (1970)
 TL 3363 (1968); 399 (1979)
 Org Syn 52 5 (1972); 55 84 (1975)
 Syn 567 (1981) (β -hydroxy ketones)
 Org Syn Coll Vol 6 373, 644 (1988)
- CrO₃·2py, Celite JOC 52 5419 (1987)
- CrO₃·3,5-dimethylpyrazole TL 4499 (1973)
- CrO₃-py-HF Syn 588 (1982)
 JOC 53 2154 (1988)
- CrO₃-*n*-BuNH₂-HCl JOC 60 2267 (1995)
- CrO₃-*n*-BuNH₂-HCl-18-crown-6 JOC 60 2267 (1995)
- CrO₃-py-HCl (PCC) TL 2647 (1975)
 Carbohydr Res 67 491 (1978); 81 187 (1980)
 Syn 245 (review), 881 (1982)
 JOC 50 2095, 2607, 2764 (1985); 52 5452 (1987); 60
 2267 (1995)
 JACS 108 4603 (1986)
- PCC-polymer JOC 43 2618 (1978)
- PCC, molecular sieves (1° benzylic, 2° alkyl or benzylic) CC 561 (1980)
 JCS Perkin I 1967 (1982)
 TL 26 3731 (1985); 28 675 (1987)
- PCC, molecular sieves, py TL 28 703 (1987)
- PCC, py Chem Phys Lipids 27 281 (1980)
- PCC, alumina Syn 223 (1980)
 JOC 47 564 (1982); 58 5452 (1993)
 TL 28 703 (1987)
 JACS 112 8090 (1990)
- PCC, silica gel JOC 54 5387 (1989)
- PCC, silica gel, ultrasound JOC 54 5387 (1989)

PCC, Celite	JOC 50 2626 (1985); 52 3662 (1987); 59 4495 (1994) TL 28 1791 (1987)
PCC, Celite, molecular sieves	TL 28 171 (1987)
PCC, NaOAc	TL 2647 (1975) JCS Perkin I 599 (1981) Syn 245 (1982) (review) JACS 108 4603 (1986); 109 5167 (1987) JOC 50 2707 (1985); 52 5452 (1987)
PCC, NaOAc, py	Chem Phys Lipids 25 381 (1979)
PCC, NaOAc, alumina	TL 28 869, 6437 (1987)
PCC, NaOAc, molecular sieves	TL 28 1073 (1987) JOC 52 4885 (1987) JACS 115 10167 (1993)
CrO ₃ -DMAP-HCl (1° allylic or benzylic, 2° allylic)	JOC 47 1787 (1982)
CrO ₃ -bipy-HCl	Syn 691 (1980)
$\left[\text{Mc} - \text{N}^+ \text{C}_4\text{H}_4 \text{NNHCOPh} \right] \text{ClCrO}_3^-$ (1° allylic; 1°, 2° benzylic)	TL 36 8513 (1995)
CrO ₃ -pyridinium polymer	Syn Commun 19 1317 (1989)
CrO ₃ , H ₂ SO ₄ , CH ₃ COCH ₃ (Jones, 1° allylic or benzylic)	JCS 39 (1946); 2548 (1953) JOC 21 1547 (1956); 25 1434 (1960); 40 1664 (1975); 54 4717 (1989) Org Syn 45 28 (1965)
(C ₅ H ₅ NH)HCrO ₄ -silica gel	Tetr 35 1789 (1979)
(n-Bu ₄ N)HCrO ₄ , HCCl ₃ (1° allylic or benzylic)	Syn 356 (1979)
Na ₂ Cr ₂ O ₇ , H ₂ O (1° allylic, 1° or 2° benzylic)	JOC 35 3589 (1970)
Na ₂ Cr ₂ O ₇ , H ₂ SO ₄ , DMSO	JOC 39 3304 (1974)
K ₂ Cr ₂ O ₇ , H ₂ SO ₄ (phase transfer)	TL 1601 (1978) JCS Perkin II 788 (1979) Syn 134 (1979)
K ₂ Cr ₂ O ₇ , DMSO or polyethylene glycol (1° allylic, 1° or 2° benzylic)	Syn 646 (1980)
K ₂ Cr ₂ O ₇ , benzene (phase transfer) (1° allylic or benzylic, 2° benzylic)	TL 4167 (1977)
K ₂ Cr ₂ O ₇ -HCl, alumina (1°, 2° alkyl; 1°, 2° benzylic; 1°, 2° allylic)	Acta Chem Scand 43 485 (1989)
K ₂ Cr ₂ O ₇ -HCl, silica (2° alkyl; 1°, 2° benzylic; 1°, 2° allylic)	Acta Chem Scand 43 485 (1989)

- (*n*-Bu₄N)₂Cr₂O₇, CH₂Cl₂ (1° allylic, 1° or 2° benzylic) *Syn Commun* 10 75 (1980)
- (PhCH₂NEt₃)₂Cr₂O₇, HMPA (1° allylic or benzylic, 2° benzylic) *Syn* 1091 (1982)
- (C₅H₅NH)₂Cr₂O₇ (PDC), CH₂Cl₂ TL 2647 (1975); 399 (1979)
JOC 41 380 (1976); 57 5178 (1992)
Ind J Chem B 22 69 (1983)
JACS 112 3497 (1990)
- PDC, cat (C₅H₅NH)O₂CCF₃ JOC 50 2981 (1987)
- PDC, HOAc, molecular sieves TL 26 1699 (1985); 28 5129 (1987)
Syn Commun 16 11 (1986)
- PDC-polymer JOC 46 1728 (1981)
- PDC, Zeolite 3A TL 31 1735 (1990)
- PDC, molecular sieves (1° or 2° benzylic, 1° allylic, 2° alkyl) CC 561 (1980)
JCS Perkin I 1967 (1982)
JACS 109 6389 (1987)
TL 28 2959 (1987)
JOC 58 165 (1993)
- cat PDC, (Me₃SiO)₂ TL 24 2185 (1983)
- cat PDC, Na₂CO₃·1.5H₂O₂, cat Adogen 464 (1°, 2° benzylic and allylic) TL 35 1989 (1994)
- $\left[\begin{array}{c} \text{H} \\ | \\ \text{N} \\ | \\ \text{N}^+ \\ | \\ \text{H} \end{array} \right]_2 \text{Cr}_2\text{O}_7^{2-}$ (1°, 2° allylic; 1° benzylic; 2° alkyl) BCSJ 59 3297 (1986)
JACS 111 2302 (1989); 115 3056 (1993)
- (Ph₃PCH₂PPh₃)Cr₂O₇ (1° allylic, 1° or 2° benzylic) TL 27 1775 (1986)
- CrO₂Cl₂, SiO₂-Al₂O₃ JOC 42 2182 (1977)
- CrO₂Cl₂, *t*-BuOH, K₂CO₃ (1° benzylic, 2° alkyl) JOC 58 512 (1993)
- CrO₂Cl₂, HOCH₂CH₂CH₂OH, K₂CO₃ (2° alkyl) JOC 58 512 (1993)
- (Phen)CrOCl₃ TL 21 1583 (1980)
- (Phen)H₂CrOCl₃ TL 21 1583 (1980)
- (py)CrO₅ TL 3749 (1977)
- n*-Bu₄N[MoO(O₂)₂(C₅H₄N(O)CO₂)] JOC 52 5467 (1987); 55 3658 (1990)
- cat Na₃PMo₂V₂O₄₀-C, air (1°, 2° benzylic) JOC 56 5707 (1991)
- [C₅H₅N(CH₂)₁₅CH₃]₃PMo₁₂O₄₀, H₂O₂ JOC 52 1868 (1987)
- cat MoO₄²⁻ or WO₄²⁻, H₂O₂, phase transfer catalyst (1° benzylic, 2° alkyl) JOC 51 2661 (1986)
- cat [(*n*-C₈H₁₇)₃NCH₃]₃PO₄[W(O)(O₂)₂]₄, H₂O₂ (1° benzylic, 2° alkyl) JOC 56 5924 (1991)

- MnO₂ (particularly allylic, benzylic and propargylic) JACS 77 4399 (1955); 107 1028, 1034 (1985); 108 2691 (1986); 109 4690, 6719 (1987); 110 4685 (1988); 111 1057 (1989); 116 82 (1994); 117 8220 (1995)
JCS 1430 (1952); 4685 (1956); 4983 (1963)
Quart Rev 13 61 (1959)
JOC 24 1051 (1959); 35 3971 (1970); 51 2863, 4158 (1986); 52 398, 3662, 5067, 5700 (1987); 57 965, 6063 (1990); 58 3018 (1993); 59 5305, 5488 (1994)
Proc Chem Soc 110 (1964)
Syn 65, 133 (1976) (reviews)
CC 1237 (1986)
TL 28 5403 (1987); 33 4187 (1992)
Org Syn Coll Vol 7 102 (1990)
- KMnO₄ (on solid support, 1° allylic or benzylic) JACS 99 3837 (1977)
TL 22 4889 (1981)
- K₂MnO₄, (PhNEt₃)Cl, NaOH (1° or 2° allylic or benzylic) TL 30 2559 (1989)
- K₂MnO₄·Al₂O₃·CuSO₄·5H₂O (1° or 2° allylic or benzylic, 2° alkyl) TL 30 2559 (1989)
- BaMnO₄·Al₂O₃·CuSO₄·5H₂O (1° or 2° allylic or benzylic, 2° alkyl) TL 30 2559 (1989)
- BaMnO₄ (1° or 2° alkyl, 1° or 2° benzylic, 1° or 2° allylic, 2° propargylic) TL 839 (1978); 23 3283 (1982); 28 5655, 5865 (1987)
BCSJ 56 914 (1983)
JACS 106 7861 (1984); 108 4953 (1986)
CC 1319 (1986)
JOC 51 4169 (1986); 59 332 (1994)
- [n-C₁₆H₃₃N(CH₃)₃]MnO₄ (1° or 2° benzylic) CL 2131 (1984)
- AgMnO₄ (1° alkyl, 1° or 2° benzylic) TL 23 1847 (1982)
- K₂FeO₄, K10 montmorillonite clay (1° benzylic and allylic; 2° alkyl) TL 36 8505 (1995)
- K₂FeO₄, Al₂O₃, CuSO₄·5H₂O (1° or 2° benzylic and allylic, 2° alkyl) TL 27 2875 (1986)
- Ag₂FeO₄ (1° or 2° benzylic and allylic) Syn Commun 16 211 (1986)
- Fe(NO₃)₃ on clay Syn 849 (1980)
- FeCl₃, hν JOC 42 171 (1977)
- cat RuO₂, NaOCl Methods Carbohydr Res 6 337 (1972)
- cat RuO₂, KIO₄, K₂CO₃ (2° alkyl) Carbohydr Res 24 192 (1972)
Methods Carbohydr Chem 7 3 (1976)
- RuO₄ (1° benzylic, 2° alkyl) JACS 80 6682 (1958)
Rev Pure Appl Chem 22 47 (1972) (review)

cat (<i>n</i> -Pr ₄ N)RuO ₄ , NMO, molecular sieves	CC 1625 (1987) TL 32 4925 (1991) J Med Chem 35 3208 (1992) JACS 114 7387 (1992) JCS Perkin I 2329 (1993) JOC 59 3113 (1994); 60 4813, 6109 (1995) Tetr 50 3235 (1994) Syn 639 (1994) (review)
cat (<i>n</i> -Bu ₄ N)RuO ₄ , NMO, molecular sieves	CC 1625 (1987)
cat RuCl ₃ ·3H ₂ O, H ₂ O ₂ , cat [(<i>n</i> -C ₁₀ H ₂₁) ₂ NMe ₂]Br (1° benzylic, 2° alkyl)	JOC 53 3553 (1988)
cat H ₂ Ru(PPh ₃) ₄ , H ₂ C=CHCH ₂ OCO ₂ Me (1° allylic, 2° alkyl or allylic)	TL 27 1805 (1986)
Co Schiff base,  CO ₂ Et, O ₂	TL 35 4007 (1994)
NiO ₂ (1° or 2° allylic, benzylic, allenic)	JOC 27 1597 (1964) Chem Rev 75 491 (1975) (review) TL 1595 (1979) JACS 104 2642 (1982)
Ni(O ₂ CPh) ₂ , Br ₂	Syn Commun 10 881 (1980)
NiBr ₂ , (PhCO ₂) ₂	JOC 44 2955 (1979)
cat Pd(OAc) ₂ , cat PPh ₃ , ArBr, NaH or K ₂ CO ₃ (1° allylic or benzylic; 2° alkyl)	JOC 48 1286 (1983)
cat Pd(OAc) ₂ , PhI, <i>n</i> -Bu ₄ NCl, NaHCO ₃ , DMF (1° alkyl or benzylic, 2° alkyl)	TL 26 6257 (1985)
cat PdCl ₂ , cat Adogen 464, Na ₂ CO ₃ (1° allylic or benzylic, 2° alkyl)	TL 36 2473 (1995)
cat Pd(PPh ₃) ₄ , O ₂ , (NH ₄)PF ₆ (1° or 2° allylic)	TL 35 7097 (1994)
CuCl, O ₂ , phenanthroline, K ₂ CO ₃ (1° allylic or benzylic, 2° benzylic)	TL 1215 (1977)
Cu(NO ₃) ₂ ·SiO ₂ (1° or 2° benzylic, 2° alkyl)	TL 29 6265 (1988) JOC 54 1531 (1989)
Ag ₂ CO ₃ , Celite	Compt Rend C 267 900 (1968) CC 1102, 1118 (1969) Tetr 29 1011 (1973) Syn 401 (1979) TL 22 3721, 3725 (1981) JOC 55 1579 (1990) JACS 112 4897 (1990)
Zn(NO ₃) ₂ ·SiO ₂ (1° or 2° benzylic, 2° alkyl)	TL 29 6265 (1988) JOC 54 1531 (1989)
cat CAN, NaBrO ₃ (1° benzylic)	Syn 936 (1978) TL 539 (1982)

<i>t</i> -BuO ₂ H, cat VO(acac) ₂	TL 24 5009 (1983)
<i>t</i> -BuO ₂ H, cat chromia-pillared montmorillonite	TL 31 5785 (1990)
<i>t</i> -BuO ₂ H, cat (PhCH ₂ NMe ₃)OMoBr ₄	TL 25 4417 (1984)
<i>t</i> -BuO ₂ H, cat [C ₃ H ₅ N(CH ₂) ₁₅ CH ₃]PMo ₁₂ O ₄₀	Syn Commun 16 537 (1986)
<i>t</i> -BuO ₂ H, cat Mo(CO) ₆ , cat [C ₃ H ₅ N(CH ₂) ₁₅ CH ₃]Cl, MgSO ₄	Syn 59 (1986)
BaMnO ₄ , Al ₂ O ₃ , CuSO ₄ ·5H ₂ O	TL 30 2559 (1989)
K ₂ FeO ₄ , Al ₂ O ₃ , CuSO ₄ ·5H ₂ O	TL 27 2875 (1986)
CAN or Ce(SO ₄) ₂ ·2H ₂ SO ₄ , NaBrO ₃	TL 23 539 (1982) JOC 50 2759 (1987)
Raney Ni	JOC 51 5482 (1986)
electrolysis, poly-4-vinylpyridine·HBr	JOC 45 5269 (1980)

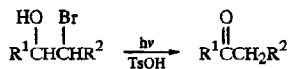
Enantioselective oxidation

baker's yeast (ArCHOHMe) TL 34 883 (1993)

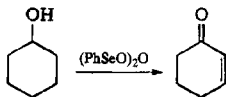
Selective oxidation, allylic or benzylic > alkyl ROH

See earlier sections.

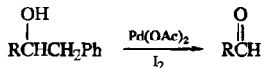
For the selective oxidation of diols, see page 1250, Section 22.



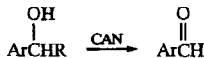
TL 33 2459 (1992)



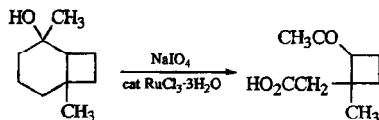
CC 952 (1978)



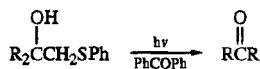
Ind J Chem B 21 408 (1982)



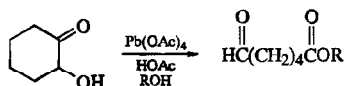
JACS 90 4755 (1968); 93 4536 (1971)
JOC 53 1504 (1988)



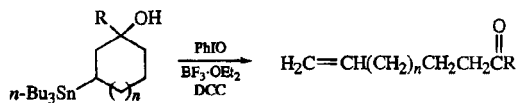
JOC 52 689 (1987)



TL 31 63 (1990)

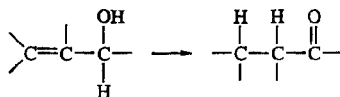


JOC 54 4083 (1989)

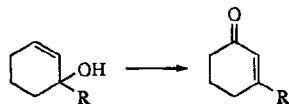
R = H ($n = 1, 2$); R = alkyl ($n = 1$), aryl ($n = 0-2$)

JOC 54 4832 (1989)

19. Allylic Alcohols

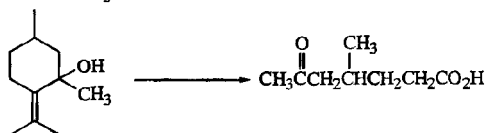
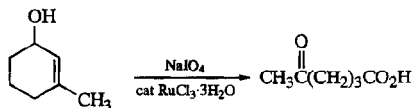


See page 1275, Section 1.

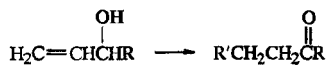
PCC, Al_2O_3

JOC 59 5983 (1994)

See page 1201, Section 1 for other oxidants.

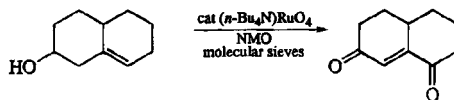


JOC 52 689 (1987)



See page 1617, Section 16.

20. Homoallylic Alcohols



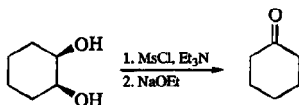
TL 32 3201 (1991)

21. Propargylic Alcohols

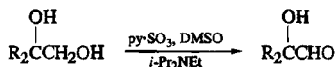
See page 1275, Section 1.

22. Diols and Derivatives

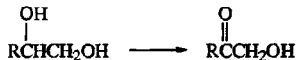
See also page 1234, Section 18 for some other selective oxidations of diols.



TL 31 463 (1990)



TL 28 1603 (1987)



TL 35 8477 (1994)



H_2O_2 , zeolite

TL 35 8477 (1994)

H_2O_2 , cat ($n\text{-C}_{16}\text{H}_{33}\text{C}_5\text{H}_4\text{N}_3\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4$)

JOC 56 6233 (1991)

$t\text{-BuO}_2\text{H}$, chromia-pillared montmorillonite

TL 31 5785 (1990)

NaOCl , HOAc

TL 23 4647 (1982)

$n\text{-Bu}_2\text{SnO}$ / NBS

J Carbohydr Chem 12 557 (1993)

$(n\text{-Bu}_3\text{Sn})_2\text{O}$ / Br_2

TL 31 6777 (1990)

Br_2 , $(n\text{-Bu}_3\text{Sn})_2\text{O}$

TL 4597 (1976)
 JCS Perkin I 1568 (1979)
 JACS 117 6224 (1995)

trichloromelamine

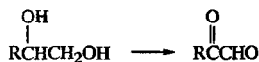
JOC 58 5003 (1993)

 $(\text{COCl})_2$, DMSO/ Et_3N $(\text{CF}_3\text{CO})_2\text{O}$, DMSO/ Et_3N

TL 36 8513 (1995) (R = aryl)

JOC 50 2198 (1985)

JOC 52 4851 (1987)

 Cl_2 , $\text{PhSMe}/\text{Et}_3\text{N}$

TL 287 (1974)

 Cl_2 , $\text{Me}_2\text{S}/\text{Et}_3\text{N}$

TL 287 (1974)

 Cl_2 , DMSO/ Et_3N

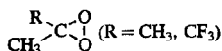
TL 287 (1974)

NCS, DMSO/ Et_3N

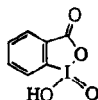
TL 287 (1974)

 $\text{py} \cdot \text{SO}_3$, DMSO/ Et_3N

JOC 36 877 (1971); 53 4864 (1988)



TL 34 4559 (1993)



TL 35 8019 (1994)

JOC 60 7272 (1995)



JOC 58 3600 (1993)

TL 36 3031 (1995)



JOC 58 3600 (1993)

 NaOCl , cat 4-MeO-TEMPO

JOC 54 2970 (1989)

 $(n\text{-Bu}_3\text{Sn})_2\text{O}$, Br_2

TL 4597 (1976)

JCS Perkin I 1568 (1979)

 $n\text{-Bu}_2\text{SnO}/\text{Br}_2$

Compt Rend C 278 1051 (1974)

 $n\text{-Bu}_2\text{SnO}/\text{Br}_2$, $n\text{-Bu}_3\text{SnOMe}$

JCS Perkin I 1568 (1979)

JACS 112 8193 (1990); 115 7593 (1993)

 $n\text{-Bu}_2\text{SnO}/\text{Br}_2$, molecular sieves

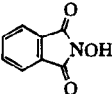

JCS Perkin I 1568 (1979)

 Ag_2CO_3 -celite

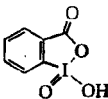
CC 1102 (1969)

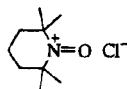
cat Cp_2ZrH_2 , R_2CO

Syn 774 (1986)

	$\begin{array}{c} \text{HO} \quad \text{OH} \\ \quad \\ \text{RCHCHR} \end{array} \longrightarrow \begin{array}{c} \text{O} \quad \text{O} \\ \quad \\ \text{RC}-\text{CR} \end{array}$	
O_2 , cat $\text{Co}(\text{acac})_3$, cat 		TL 36 6923 (1995)
H_2O_2 , cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3(\text{PO}_4[\text{W}(\text{O})(\text{O}_2)_2]_4)$		TL 36 1523 (1995)
<i>t</i> -BuO ₂ H, cat $(\text{PhCH}_2\text{NMe}_3)\text{OMoBr}_4$		TL 25 4417 (1984)
<i>n</i> -Bu ₄ N[MoO(O ₂) ₂ (C ₅ H ₄ N(O)CO ₂)]		JOC 55 3658 (1990)
NaOCl, cat 4-MeO-TEMPO		JOC 54 2970 (1989)
(4-AcNH-TEMPO)OTs, TsOH		JOC 59 6338 (1994)
4-PhCO ₂ -TEMPO, electrolysis		SL 57 (1990)
		JOC 56 2416 (1991)
		TL 35 8019 (1994)
Ac ₂ O, DMSO		JOC 32 66 (1967)
		CC 1537 (1971)
(CF ₃ CO) ₂ O, DMSO/Et ₃ N		JOC 52 4851 (1987)
py·SO ₃ , DMSO		JACS 95 242 (1973); 97 3468 (1975)
PhCH=CHCOCH ₃ , cat RuCl ₂ (PPh ₃) ₃		JOC 37 1832 (1972)

	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{RCH}(\text{CH}_2)_n\text{CHR} \end{array} \longrightarrow \begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{RCH}(\text{CH}_2)_n\text{CR} \end{array}$	
<u>Reagent(s)</u>	<u><i>n</i></u>	
$\text{CH}_3\text{C}(\text{O})\text{CH}_3$	1, 2	TL 36 3031 (1995)
Ag ₂ CO ₃ -celite	1, 2	CC 1102 (1969)
cat Cp ₂ ZrH ₂ , R ₂ CO	2	Syn 774 (1986)

	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{RCH}-\text{C}_n-\text{CH}_2 \end{array} \longrightarrow \begin{array}{c} \text{OH} \quad \text{O} \\ \quad \\ \text{RCH}-\text{C}_n-\text{CH} \end{array}$	
	$n \geq 1$	
		TL 36 7945 (1995)
NaOCl, cat TEMPO		JOC 54 2970 (1989)
		TL 31 2177 (1990)
NaBr, cat 4-PhCO ₂ -TEMPO, electrolysis		JOC 56 2416 (1991)



JOC 58 832 (1993)

NaBrO₂, cat 4-PhCO₂-TEMPO

JOC 55 462 (1990)

cat Cp₂ZrH₂, R₂CO

Syn 774 (1986)

quinolinium chlorochromate

Chem Ind 751 (1986)

RuCl₂(PPh₃)₃

TL 22 1605 (1981)

cat RuCl₂(PPh₃)₃, (Me₃SiO)₂

TL 24 2185 (1983) (1° allylic or benzylic)

 $n \geq 1$

NBA

JACS 74 483 (1952); 76 3682 (1954)

NBS, H₂O

JACS 109 3017 (1987)

Cl₂, py

TL 3059 (1974)

Cl₂ or Br₂, HMPA

Syn 811 (1976)

Br₂, (n-Bu₃Sn)₂O

TL 4597 (1976)

JCS Perkin I 1568 (1979)

NaOCl, HOAc

JOC 45 2030 (1980)

TL 23 4647 (1982)

NaBrO₂, HOAc, H₂O

Syn 815 (1983)

JOC 58 1483 (1993)

NaBrO₃, Ce-polymer

TL 25 3317 (1984)

NaBrO₃, CAN

TL 23 539 (1982)

JOC 50 2759 (1987)

NaBrO₃, cat Ce(SO₄)₂·2H₂SO₄

TL 23 539 (1982)

H₂O₂, zeolite

TL 35 8477 (1994)

H₂O₂, cat (NH₄)₆Mo₇O₂₄·4H₂O, n-Bu₄NCl, K₂CO₃

TL 25 173 (1984)

H₂O₂, [C₅H₅N(CH₂)₁₅CH₃]₃PMo₁₂O₄₀

JOC 52 1868 (1987)

H₂O₂, cat [C₅H₅N(CH₂)₁₅CH₃]₃PW₁₂O₄₀

JOC 53 3587 (1988)

t-BuO₂H, cat VO(acac)₂

TL 24 5009 (1983)

t-BuO₂H, cat chromia-pillared montmorillonite

TL 31 5785 (1990)

t-BuO₂H, cat (PhCH₂NMe₃)OMoBr₄

TL 25 4417 (1984)

t-BuO₂H, cat [C₅H₅N(CH₂)₁₅CH₃]₃PMo₁₂O₄₀

Syn Commun 16 537 (1986)

t-BuO₂H, cat Mo(CO)₆, cat [C₅H₅(CH₂)₁₅CH₃]Cl, MgSO₄

Syn 59 (1986)

K_2MnO_4 , Al_2O_3 , $CuSO_4 \cdot 5H_2O$

TL 30 2559 (1989)

 $BaMnO_4$, Al_2O_3 , $CuSO_4 \cdot 5H_2O$

TL 30 2559 (1989)

 K_2FeO_4 , Al_2O_3 , $CuSO_4 \cdot 5H_2O$

TL 27 2875 (1986)



TL 36 8513 (1995) (R = aryl)

 Ag_2CO_3 , celite

CC 1102 (1969)



TL 35 8477 (1994)

 Al_2O_3 , PhCHO

TL 3499 (1976)

 $(Ph_3C)BF_4$

JACS 98 7882 (1976)

TL 2771 (1978)

electrolysis, poly-4-vinylpyridine·HBr

JOC 45 5269 (1980)

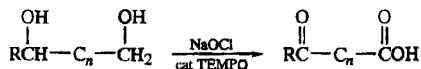


NaOCl, cat TEMPO

JOC 54 2970 (1989)

electrolysis, TEMPO

JACS 105 4492 (1983)



JOC 54 2970 (1989)



Reagent

 \underline{n} $RuCl_2(PPh_3)_3$

4

JACS 106 1148 (1981)

5

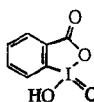
TL 28 3123 (1987)

JOC 57 5058 (1992)

 $BaMnO_4$

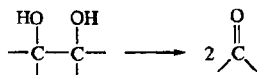
4

JCS Perkin I 1579 (1983)



4, 5

TL 36 3485, 7945 (1995)



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 5.3, p 703

 $Pb(OAc)_4$

Ann 599 81 (1956)

Newer Methods Prep Org Chem 2 367 (1963)

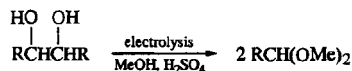
TL 27 5853 (1986); 28 2999 (1987); 36 1027 (1995)

JOC 56 5834 (1991); 57 3365 (1992)

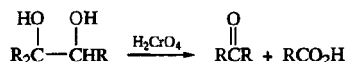
 $NaBiO_3$, H_3PO_4 , H_2O

JCS 1907 (1950)

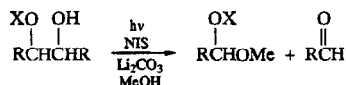
(<i>p</i> -Tol ₃ BiO) _n	TL 35 8197 (1994)
Ca(OC ₂) ₂ , H ₂ O, CH ₃ CN, HOAc	TL 23 3135 (1982)
NBS, <i>n</i> -Bu ₄ NI, <i>hν</i>	JOC 60 6602 (1995)
NIS	JOC 46 1927 (1981)
HIO ₄	Org Rxs 2 341 (1944) (review)
NaIO ₄ , H ₂ O	TL 24 1377 (1983); 28 3035 (1987) JACS 109 3353 (1987) JOC 54 3738 (1989)
NaIO ₄ , silica gel	JCS Perkin I 2970 (1981)
NaIO ₄ , NaHCO ₃	JOC 56 4056 (1991)
NaIO ₄ , NaOH	JOC 50 2095 (1985)
NaIO ₄ -Amberlite 904	JCS Perkin I 509 (1982)
NaIO ₄ , cat (<i>n</i> -Bu ₄ N)IO ₄ , NaOAc, H ₂ O, CH ₂ Cl ₂	JOC 55 1670 (1990)
I(OAc) ₃	JCS Perkin I 1483 (1978)
H ₂ CrO ₄	JACS 82 1401 (1960); 84 1252, 2241 (1962)
PCC	Syn Commun 12 833 (1982)
MnO ₂	Acta Chem Scand 15 849 (1961) JCS C 369 (1970) Angew 85 401 (1973) Angew Int 12 401 (1973)
cat iron-porphyrin, 1-benzyl-1,4-dihydronicotinamide	JACS 110 1187 (1988)
HgO, I ₂	JOC 51 5446 (1986)
(NH ₄) ₄ [Ce(SO ₄) ₄]·2H ₂ O, H ₂ SO ₄	JACS 81 1494 (1959)
electrolysis	JACS 97 2546 (1975)



JOC 46 3312 (1981)

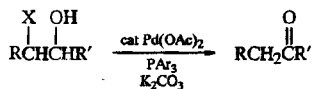


TL 29 6403 (1988)

X = alkyl, SiR₃

TL 31 6285 (1990)

23. Halohydrins

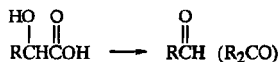


TL 23 3085 (1982)

24. α -Hydroxyketones

See page 1661, Section 18.

25. Hydroxyacids and Derivatives

NBS, *n*-Bu₄NI, *h* ν

JOC 60 6602 (1995)

NIS

JOC 47 3006 (1982)

NaIO₄, H₂O, HOAc, CH₃COCH₃

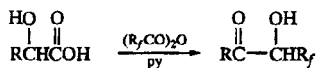
TL 1725 (1968)

(n-Bu₄N)IO₄

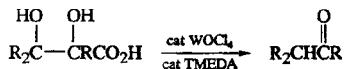
Syn 563 (1980)

NaBiO₃

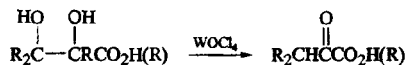
JCS 1907 (1950)



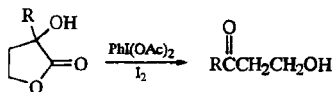
TL 35 8209 (1994)



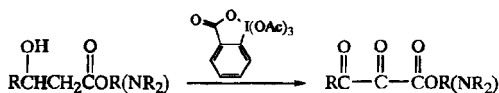
TL 33 6787 (1992)



TL 33 6791 (1992)

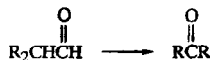


TL 36 2141 (1995)



TL 34 167 (1993)

26. Aldehydes

air, Cu(OAc)₂, DABCO, bipy

TL 985 (1969); 35 2295 (1994)

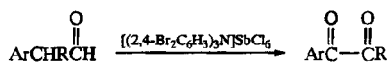
O₂, KOH, *t*-BuOH

Ber 100 259 (1967)

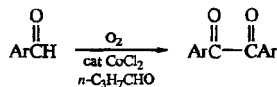
O₂, KO-*t*-Bu, *t*-BuOH

Ber 100 259 (1967)

JOC 57 3173 (1996)

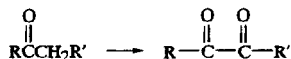


TL 34 3897 (1993)



TL 35 2959 (1994)

27. Ketones

SeO₂

Org Rxs 5 331 (1949); 24 261 (1976) (reviews)

JOC 52 2602 (1987)

KMnO₄, KOH, *n*-Bu₄NBr

TL 32 5283 (1991)

PCC

TL 32 5283 (1991)

CuBr₂/KI, DMSO, Na₂CO₃

JOC 40 1990 (1975)

t-BuOCH(NMe₂)₂/O₂, hν

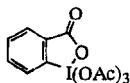
JOC 50 3573 (1985)

DDQ

TL 32 5283 (1991)

O₂, rose bengal, hν, *n*-Bu₄NF

JACS 104 4695 (1982)

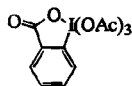


TL 34 167 (1993)

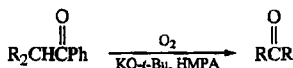
See also page 1229, Section 10.

XReagent(s)

OR

 NaNO_2 , $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ /TiCl₃ JOC 57 3546 (1992)OR, NR₂

TL 34 167 (1993)

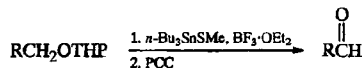


Ann 1322 (1974)

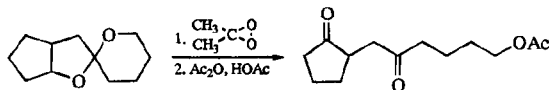
Chem Pharm Bull 26 2217 (1978); 27 222 (1979)

JOC 60 7192 (1995)

28. Acetals



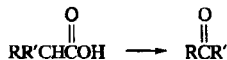
TL 30 1665 (1989)



TL 35 935 (1994)

29. Carboxylic Acids

For hydroxyacids, see page 1256, Section 25.

2 LDA/(MeS)₂/NCS, ROH

JACS 99 3101 (1977); 107 8066 (1985); 109 4626 (1987)

2 LDA/(PhS)₂/electrolysis

TL 1045 (1979)

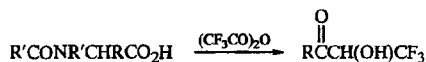
2 LDA/O₂/Me₂NCH(OMe)₂

TL 4611 (1975)

JACS 116 1776 (1994)

(n-Bu₄N)IO₄ (R = Ar)

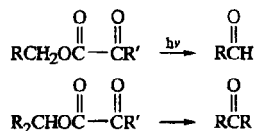
TL 21 2655 (1980)



TL 35 149 (1994)

30. Esters

See page 1256, Section 25, for hydroxyesters and page 1257, Section 27 for ketoesters.



R'

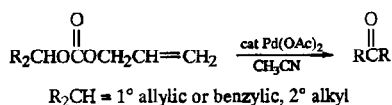
CH_3

JOC 42 1216 (1977)

JACS 111 1861 (1989)

2,4-(MeO)₂C₆H₃

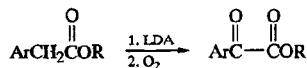
JOC 60 2461 (1995)



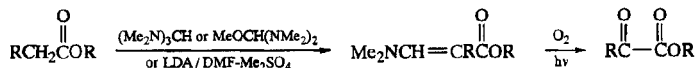
TL 25 2791 (1984)



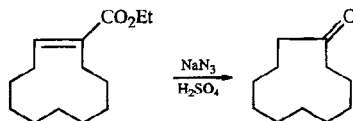
SL 289 (1993)



SL 49 (1994)



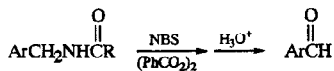
JOC 50 3573 (1985)



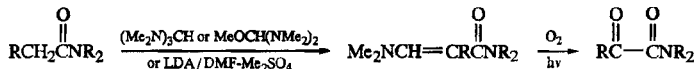
Org Syn Coll Vol 6 368 (1988)

31. Amides

See page 1256, Section 25 for hydroxyamides and page 1257, Section 27 for ketoamides.

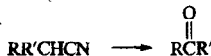


TL 3875 (1979)



JOC 50 3573 (1985)

32. Nitriles

base, O₂ (R = Ar)

Tetr 3 97 (1958)

TL 657 (1964)

K₂CO₃, air, DMSO (R = R' = Ar)

Org Prep Proc Int 2 137 (1970)

JOC 48 4097 (1983)

NaOH, O₂, (Et₃NCH₂Ph)Cl

Syn 1009 (1980)

LDA / *t*-BuMe₂SiCl / I₂ / Ag₂O (R = Ar)

JOC 39 2799 (1974)

LDA / O₂ / SnCl₂ / NaOH

JOC 40 267 (1975)

LDA / O₂ / Na₂SO₃, buffer

TL 28 2087 (1987)

LiNCy(*i*-Pr), air, DMSO

JOC 48 4097 (1983)

LDA / PhSeCl / NBS, H₂O

TL 3029 (1974)

t-BuO₂H, cat RuCl₂(PPh₃)₃ / TiCl₄

SL 62 (1989)

PCl₅ / NaOH

TL 437 (1967); 2301 (1973)

JOC 33 2211 (1968)

JACS 109 7270 (1987)

33. Furans

Br₂, H₂O

TL 26 3039 (1985)

Br₂, MeOH / H₃O⁺

J Heterocyclic Chem 9 523 (1972)

Austral J Chem 30 2561 (1977)

PCC

Tetr 36 661 (1980)

m-ClC₆H₄CO₂H

JOC 46 4143 (1981)

TL 26 1367 (1985)

electrolysis, MeOH / H₃O⁺

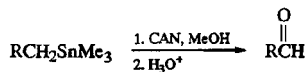
J Heterocyclic Chem 9 523 (1972)

magnesium monoperoxyphthalate hexahydrate

TL 31 7669 (1990)

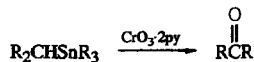
34. Organometallics

For the oxidation of organoboranes, see also page 1207, Section 2.



SL 402 (1992)

JACS 114 3115 (1992)



JACS 99 4836 (1977)

JOC 58 2972 (1993) (enone)



M

Reagents

B

H₂O₂, base

JACS 83 3834 (1961); 89 5086
(1967); 91 4771 (1969); 94
4370 (1972)

Org Rxs 13 1 (1963)

TL 41 (1970)

Organomet Chem Syn 1 249
(1971)

JOC 38 1617 (1973)

Si

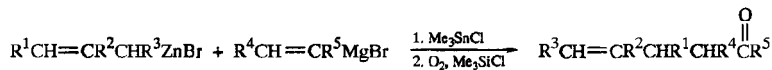
H₂O₂, base

Organomet 2 1694 (1983)

JACS 111 4984 (1989)

Me₃NO, KHF₂

TL 27 75 (1986)



TL 29 6697 (1988)

3. REDUCTION OF PHENOLS, CARBOXYLIC ACIDS AND DERIVATIVES, AND NITRILES

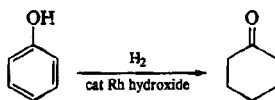
Reviews:

Org Rxs 36 249 (1988) (alkoxyaluminum hydrides)

Org Prep Proc Int 2/ 451 (1989) (metal hydride reduction of acids and derivatives to aldehydes)

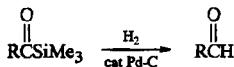
1. Phenols

See also page 1617, Section 16.



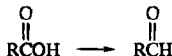
J Catalysis 8 100 (1967); 12 214 (1968)

2. Acylsilanes



TL 32 457 (1991)


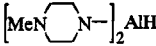


3. Carboxylic Acids

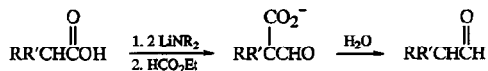


Reviews:

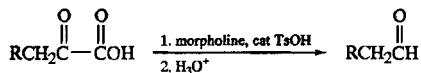
Org Rxs 8 218 (1954)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 8, Parts 1.11 and 1.12, pp 259-306

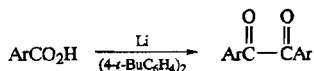
- Li, RNH₂ (R = Me, Et)/NH₄Cl/H₃O⁺ JOC 28 2918 (1963)
IACS 92 5774 (1970)
- BH₃·SMe₂/PCC Syn 704 (1979)
- (CH₃)₂CHC(CH₃)₂BH₂ JOC 37 2942 (1972)
- (CH₃)₂CHC(CH₃)₂BHCl·SMe₂ JACS 106 8001 (1984)
JOC 51 5264 (1986); 52 5400 (1987)
- (CH₃)₂CHC(CH₃)₂BHBr·SMe₂ JOC 52 5030 (1987)
TL 28 2389 (1987)
- 9-BBN/LiH₂B  TL 28 4575 (1987)
- 9-BBN/*t*-BuLi/9-BBN TL 28 6231 (1987)
- t*-Bu₂AlH J Gen Chem USSR 34 1021 (1964)
-  AlH CL 1447 (1974)
JOC 49 2279 (1984)
- SOCl₂/piperidine/NaH₂AlEt₂ Syn Commun 23 1775 (1993)
- PhSiH₂CH₂NMe₂  , 
or *o*-PhSiH₂C₆H₄CH₂NMe₂; Δ TL 28 3941 (1987)
- i*-BuMgBr, Cp₂TiCl₂ Syn 871 (1981)
- (Me₂N=CHCl)Cl/LiHAl(O-*t*-Bu)₃ Org Syn Coll Vol 8 498 (1993)
- (Me₂N=CHCl)Cl/LiHAl(O-*t*-Bu)₃, cat CuI TL 24 1543 (1983)
- o*-HSC₆H₄OH, POCl₃, HClO₄/LiAlH₄/H₂O, HgCl₂ J Heterocyclic Chem 11 943 (1974)
- o*-C₆H₄(NH₂)₂, PPA/NaOEt/MeI/NaBH₄ or
LiAlH₄/H₃O⁺ Syn 303 (1981)
- PPh₃, electrolysis (α-amino acids) TL 33 1347 (1992)



TL 699 (1970)



TL 23 459 (1982)



TL 30 6267 (1989)

4. Acid Halides

H₂, cat Pd, BaSO₄ (Rosenmund)

Ber 51 585 (1918); 54 425 (1921)

Org Rxs 4 362 (1948)

Rec Trav Chim 90 1323 (1971); 100 21 (1981)

JACS 108 2608 (1986)

H₂, cat Pd-C, NaOAc, Quinoline S

Org Syn Coll Vol 6 1007 (1988)

H₂, cat Pd-C, 2,6-lutidine

Syn 767 (1976)

JACS 108 2608 (1986)

JOC 59 3738 (1994)

H₂, cat PdCl₂(PPh₃)₂, R'₃N (R = aryl)

JACS 96 7761 (1974)

Mg, CdCl₂, H₂O

TL 34 1681 (1993)

NaBH₄, DMF, -70 °C

TL 22 11 (1981)

NaBH₄, py, DMF, 0 °C

Syn Commun 12 839 (1982)

NaBH₄, CdCl₂

CC 354 (1978)

JCS Perkin I 27 (1980)

(Ph₃P)₂CuBH₄

TL 1437, 2473 (1978); 975 (1979)

JOC 45 3449 (1980)

JACS 112 265 (1990)

[(Ph₃P)₂CuBH₃CN]₂

TL 21 813 (1980)

LiAlH(O-*i*-Bu)₃

JACS 79 252 (1956); 80 5377 (1958)

J Lipid Res 8 380 (1967)

Syn 217 (1972)

Org Syn Coll Vol 6 529 (1988)

TL 36 7281 (1995)

NaAlH(O-*i*-Bu)₃

JOC 58 4732 (1993)

piperidine / NaH₂AlEt₂

Syn Commun 23 1775 (1993)

Et₃SiH, cat Pd-C

JOC 34 1977 (1969)

Et₃SiH, cat PtCl₂(PPh₃)₂ or ClRh(CO)(EtPPh₂)₂

CC 1703 (1970)

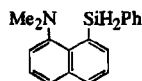
JCS Dalton 2460, 2646 (1975)

polymethylhydrosiloxane, cat RhCl₃,
cat [(*n*-C₈H₁₇)₃NCH₃]Cl

J Mol Catal 37 359 (1986)

o-Me₂NCH₂C₆H₄SiH₂Ph

TL 29 1271 (1988)





TL 29 1271 (1988)

n-Bu₃SnH

JOC 25 284 (1960)

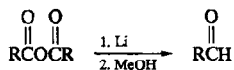
JACS 88 571 (1966)

$n\text{-Bu}_3\text{SnH}$, cat $\text{Pd}(\text{PPh}_3)_4$	CC 432 (1980) JOC 46 4439 (1981)
$\text{Na}_2\text{Fe}(\text{CO})_4/\text{HOAc}$	BCSJ 44 2569 (1971) JACS 94 2516 (1972)
$(\text{Me}_4\text{N})\text{HFe}(\text{CO})_4$	TL 781 (1977)
$o\text{-HOC}_6\text{H}_4\text{SH}$, $\text{HBF}_4/\text{NaBH}_4/\text{H}_2\text{O}$, HgCl_2	JCS Perkin I 323 (1976)
 $\text{NH}/i\text{-Bu}_2\text{AlH}$	JCS Perkin I 2470 (1980)
$\text{PhNHN}=\text{C}(\text{SMe})\text{NHPh}/\text{NaBH}_4/\text{HCl}$, H_2CO	Tetr 32 2549 (1976)
DMBI, HOAc	JOC 51 5400 (1986)
 $\text{Et}_3\text{N}/\text{H}_2\text{O}$ ($\text{R} = \text{aryl}$)	CC 459 (1975)
$n\text{-Bu}_3\text{P}/\text{Zn-Cu}$, MeSO_3H	TL 36 2247 (1995)

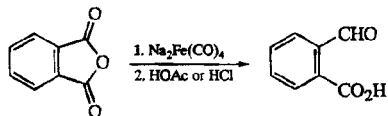


See page 1389, Section 2.6.

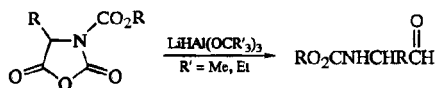
5. Anhydrides



TL 33 3737 (1992)

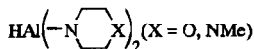
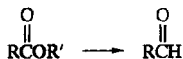


TL 3535 (1973)



TL 35 9031 (1994)

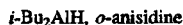
6. Esters



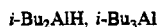
CL 215 (1975)



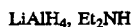
TL 619 (1962); 1779 (1969); 27 2103 (1986)
 Bull Acad Sci USSR, Div Chem Sci 288 (1963)
 JOC 40 3495 (1975); 48 2775 (1983); 52 2361
 (1987); 58 6843 (1993)
 Syn 617 (1975) (review)
 JACS 107 199 (1985); 116 9019 (1994)
 SL 386 (1993)



Bull Korean Chem Soc 10 117 (1989)



JOC 57 5469 (1992); 59 4596 (1994)



JOC 52 5486 (1987); 55 1692 (1990)



TL 2087 (1963)



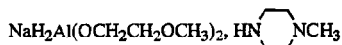
TL 619 (1962)



JACS 95 7501 (1973)



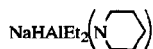
JOC 53 1828 (1988)



Syn 526 (1976)

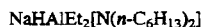


JOC 31 283 (1966)

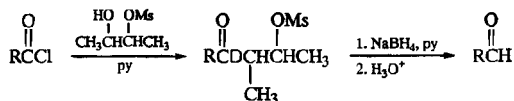


Bull Korean Chem Soc 12 7 (1991)

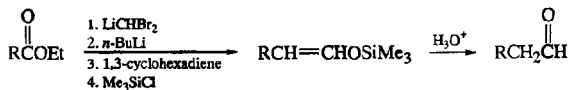
JOC 58 1941 (1993)



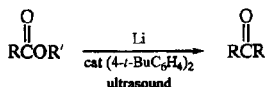
Bull Korean Chem Soc 14 522 (1993)



Org Syn Coll Vol 6 312 (1988)

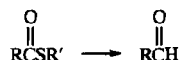


JACS 108 1325 (1986)



TL 30 4935 (1989)

7. Thioesters



hv, 1,4-cyclohexadiene (R' = 2-naphthyl)

JOC 59 2608 (1994)

Li/MeOH (R' = 2-pyridyl)

TL 33 3737 (1992)

Raney Ni

Org Rxs 8 229 (1954) (review)

i-Bu₂AlH

CC 330 (1978)

TL 34 8163, 8167 (1993)

JOC 58 3787 (1993)

NaH₂Al(OCH₂CH₂OCH₃)₂ (on ester enolate)

JOC 53 1828 (1988)

Et₃SiH, cat Pd-C

JACS 112 7050 (1990); 115 8451, 11446 (1993)

JOC 58 2313, 2369 (1993)

TL 34 2229 (1993)

Et₃SiH, cat Pd-CaCO₃-PbO

JACS 115 4497 (1993)

n-Bu₃SnH, cat Pd(PPh₃)₄

TL 34 2491 (1993)

XReagents

R

PhP(CH₂CH₂CH₂NMe₂)₂, LiBr

Helv 54 710 (1971)

Org Syn Coll Vol 6 776 (1988)

n-Bu₃P, Et₃N, LiClO₄

Helv 54 710 (1971)

R, OR

Ph₃P, KO^tMe₂Et

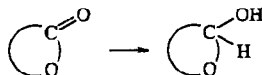
Helv 54 710 (1971)

8. Selenoesters



JOC 57 1429 (1992)

9. Lactones

(Sia)₂BIH

JOC 51 5032 (1986)

TL 28 1073 (1987)

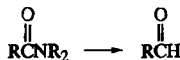
i-Bu₂AlH

Helv 46 2799 (1963)

JOC 30 3564 (1965); 50 2489 (1985); 52 4603, 4647, 4898, 5700 (1987)

- JACS 91 5675 (1969); 97 2287 (1975)
 Syn 617 (1975) (review)
 TL 27 6341, 6345 (1986); 28 221 (1987)
 NaH₂Al(OCH₂CH₂OCH₃)₂, EtOH Syn 526 (1976)
 polymethylhydrosiloxane, cat (*p*-ClC₆H₄O)₂TiCp₂, JACS 117 12641 (1995)
 cat *n*-Bu₄NF-alumina

10. Amides and Imides



Review: Org Rxs 8 252 (1954)

Amide

general

Reagent(s)

Na, NH₃, HOAc

Austral J Chem 8 512 (1955)

LiH₂Al(OEt)₂

JACS 86 1089 (1964)

LiAl(OEt)₃

JACS 86 1089 (1964)

HAL(-N(CH₃)₂)₂

CL 875 (1975)

-NH₂

LiAl(NEt₂)₃

TL 32 6903 (1991)

-N(CH₃)₂

Li, NH₃, *t*-BuOH

JOC 53 1922 (1988)

(Sia)₂BH

JACS 92 7161 (1970)

ROTF (R = Me, Et) /

JCS Perkin I 757 (1990)

LiHB(*sec*-Bu)₃

JACS 114 3125 (1992)

NaAlH₄

Tetr 25 5555 (1969)

LiAlH₄

JOC 58 4727 (1993)

LiH₂Al(OEt)₂

Ber 84 625 (1951)

LiH₂Al(OEt)₂

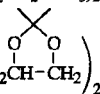
JACS 81 502 (1959); 86 1089

LiH₂Al(OEt)₂

(1964)

LiH₂Al(OCH₂CH₂OCH₃)₂


JOC USSR 13 1081 (1977)

LiH₂Al()₂

JOC USSR 13 1081 (1977)

LiAl(OEt)₃

JACS 86 1089 (1964)

NaHAIEt₂()

JOC 58 1941 (1993)

electrolysis

JOC 57 1061 (1992)

-N<

LiAlH₄

JACS 83 2016, 4549 (1961)

-N<

LiAl(O-*t*-Bu)₃

Ann 654 119 (1962)

LiAlH₄

JOC 35 458 (1970)

LiAlH₄

Org Rxs 8 252 (1954)

LiAlH₄

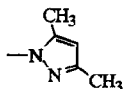
Angew 70 165 (1958)

LiAlH₄

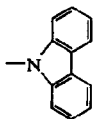
Ann 654 119 (1962)

LiAlH₄

Angew Int I 351 (1962)


AmideReagent(s)LiAlH₄

Angew 70 165 (1958)
 Ann 622 37 (1959)
 J Med Chem 20 510 (1977)
 TL 23 525 (1982); 28 3123
 (1987)

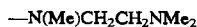
LiAlH₄


Ann 577 11 (1952)
 JOC 18 1190 (1953)



NaH₂Al(OCH₂CH₂OCH₃)₂
 EtOH or HN  NCH₃?

JOC 51 3566 (1986)



NaH₂Al(OCH₂CH₂OCH₃)₂
 EtOH or HN  NCH₃?

JOC 51 3566 (1986)



LiHAl(*i*-Bu)₂(*n*-Bu)
 NaH₂AlEt₂

JOC 49 1717 (1984)
 Bull Korean Chem Soc 13 199,
 341 (1992)



NaH₂Al(OCH₂CH₂OCH₃)₂
 LiAlH₄

TL 3303 (1968)
 Angew 64 458 (1952); 65 525
 (1953); 66 174 (1954)
 Ber 88 301 (1955); 92 528
 (1959)

i-Bu₂AlH

Bull Acad Sci USSR, Div Chem
 Sci 2046 (1959)



review
i-Bu₂AlH

Org Prep Proc Int 25 15 (1993)
 TL 22 3815 (1981)

JOC 54 4224 (1989); 57 1067,
 1070 (1992); 58 471 (1993);
 59 3113 (1994)

JACS 114 9434 (1992); 115
 3966 (1993)

SL 700 (1995)

TL 22 3815 (1981); 28 1857
 (1987); 30 3779 (1989); 35
 1181 (1994)

Syn 676 (1983)

JACS 107 7790 (1985); 112

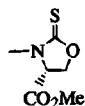
3475 (1990); 114 6570 (1992)

JOC 56 4161 (1991); 60 1727
 (1995)

Org Syn Coll Vol 8 68 (1993)

LiAlH₄

JOC 54 3824 (1989); 55 2829
 (1990); 60 4602 (1995)

 $i\text{-Bu}_2\text{AlH}$

JOC 54 3988 (1989)

 $i\text{-Bu}_2\text{AlH}$

CL 1443 (1977)

BCSJ 52 555 (1979)

JCS Perkin I 2470 (1980)

BCSJ 52 555 (1979)

 $\text{LiAl}(\text{O-}i\text{-Bu})_3$ 

JCS 584 (1936)

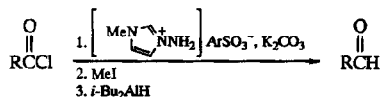
Org Rxs 8 232 (1954) (review)

JOC 26 3664 (1961)

CC 793 (1978)



Tetr 29 3985 (1973)



TL 36 455 (1995)

11. Nitriles

 $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$, Raney Ni, py, H_2O , HOAc

JCS 3961 (1962)

Montash 94 1262 (1963)

Syn Commun 20 459 (1990)

JACS 114 10181 (1992)

 $(\text{Et}_3\text{NH})\text{H}_2\text{PO}_2 \cdot 1.5\text{H}_2\text{O}$, Raney Ni

JOC 54 949 (1989)

 HCO_2H , Raney Ni

JCS 5880 (1964); 5775 (1965)

Org Syn Coll Vol 6 631 (1988)





 SnCl_2 , $\text{HCl}/\text{H}_2\text{O}$ (Stephen)

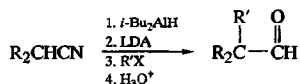
JCS 125 1874 (1925); 127 1874 (1925); 1686 (1956)

Org Rxs 8 246 (1954) (review)

Org Syn Coll Vol 3 626 (1955)

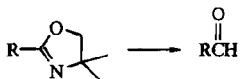
JOC 28 695 (1963)

- LiHBEt₃ (R = aryl only) JOC 45 1 (1980)
- K[BHSia] (R = aryl) TL 30 3677 (1989)
- i*-Pr₂AlH/H₂O Angew Int 12 497 (1973)
- i*-Bu₂AlH/H₂O Proc Acad Sci USSR, Chem Sec 116 879 (1958)
JOC 24 627 (1959); 29 3046 (1964); 35 186, 858 (1970); 37 2138 (1972); 41 3512 (1976); 46 4600 (1981); 50 2026, 2443 (1985); 52 28, 4191 (1987); 57 3347 (1992)
Rec Trav Chim 85 343 (1966)
Syn 617 (1975) (review)
JACS 107 7524 (1985); 108 4614 (1986); 114 9877 (1992)
Bull Korean Chem Soc 7 323 (1986)
TL 31 3669 (1990)
SL 479 (1991)
- LiAl(OEt)₃/H₂O TL (3) 9 (1959)
JACS 86 1085 (1964)
Bull Korean Chem Soc 7 323 (1986)
- LiH₂Al(OEt)₂/H₂O JACS 86 1085 (1964)
JOC 44 4603 (1979)
- NaH₂AlEt₂/H₃O⁺ Bull Korean Chem Soc 7 323 (1986); 13 199 (1992)
- NaH₂AlEt₂, Et₂AlO-/H₃O⁺ Bull Korean Chem Soc 7 323 (1986)
- LiAlH₄/H₃O⁺ Bull Korean Chem Soc 7 323 (1986)
- NaHAlEt₂() (R = aryl) Bull Korean Chem Soc 14 302 (1993)
JOC 58 1941 (1993)
- LiHAl(NR₂)₃ (R = Et, *n*-Bu, *n*-Hex) Bull Korean Chem Soc 13 451 (1992)
- (CO)₄Fe-, hv/H₃O⁺ JOC 46 3372 (1981)
- (Et₃O)BF₄/Et₃SiH/H₂O CC 45 (1974)
JOC 46 602 (1981)
- i*-PrCl, FeCl₃/Et₃SiH/H₂O JOC 46 602 (1981)



JOC 46 5250 (1981)

12. 4,5-Dihydrooxazoles



Review: *Tetr* 41 837 (1985)

MeI/NaBH₄/H₃O⁺

J Heterocyclic Chem 3 531 (1966)

Syn Commun 10 17 (1980)

MeOTf/NaBH₄/H₃O⁺

JACS 114 1010 (1992)

MeOSO₃F/NaBH₄/H₃O⁺

JACS 106 1865 (1984)

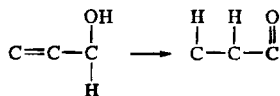
***i*-Bu₂AlH or Li-NH₃/NCS, alumina, silica or**

JOC 48 4053 (1983)

***t*-BuMe₂SiCl, NCS, KO₂, H₃O⁺**

4. REARRANGEMENTS

1. Isomerization

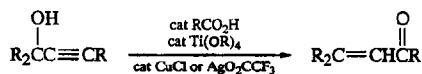


cat Mo(N ₂) ₂ (dppe) ₂	JOMC 252 105 (1983)
cat Fe(CO) ₅	IOC 32 2356 (1967)
cat CpRuCl(PPh ₃) ₂	TL 32 3039 (1991)
cat CpRuCl(PPh ₃) ₂ , (Et ₃ NH)PF ₆	TL 34 5459 (1993)
	JACS 115 2027 (1993)
cat (indenyl)RuCl(PPh ₃) ₂ , (Et ₃ NH)PF ₆	JACS 115 2027 (1993)
cat RuCl ₂ (PPh ₃) ₃ , K ₂ CO ₃	TL 34 5459 (1993)
cat [RuCl ₂ (<i>p</i> -cymene)] ₂ , K ₂ CO ₃	TL 34 5459 (1993)
cat RuCl ₃	Compt Rend C 1257 (1973)
cat RuCl ₃ , cat NaOH	CC 594 (1980)
cat [RuH(OC ₅ Ph ₄)(CO) ₂] ₂	TL 34 5459 (1993)
cat RuHCl(PPh ₃) ₃	TL 4133 (1974)
cat Ru(OTf) ₂ ·6H ₂ O	Organomet 13 224 (1994)
cat HRh(CO)(PPh ₃) ₃ , diop	Gazz Chim Ital 106 1131 (1976)
cat RhCl ₃ ·3H ₂ O-Dowex [®] 1	TL 35 781 (1994)
cat H ₂ Rh(PPh ₃) ₄	JOMC 297 C37 (1985)
cat [CIRh(CO) ₂] ₂ , NaOH (phase transfer)	IOC 45 2269 (1980)
cat Rh(ClO ₄)(BINAP)(CH ₃ OH) ₂ (enantioselective)	TL 28 4719 (1987)

cat Rh(ClO ₄)(BINAP)(COD)	Pure Appl Chem 57 1845 (1985) JACS 113 958 (1991)
cat [Rh(COD) ₂]BF ₄ , cat PPh ₃	JOC 60 3045 (1995)
<i>n</i> -BuLi / cat [Rh(dppe)]ClO ₄ / H ₂ O	TL 33 6187 (1992)
cat [Ir(COD)(Ph ₂ PMe) ₂]PF ₆	Nouv J Chim 2 355 (1978)
<i>n</i> -BuLi / cat NiCl ₂ (PCy ₃) ₂ / H ₂ O	TL 33 6187 (1992)

Catalyst

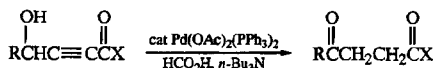
(indenyl)RuCl(PPh ₃) ₂ , InCl ₃ , (Et ₃ NH)PF ₆ , NH ₄ PF ₆	JACS 117 9586 (1995)
IrH ₅ (<i>i</i> -Pr ₃ P) ₂	TL 30 2109 (1989) JCS Perkin I 1921 (1993)
Pd ₂ (DBA) ₃ ·CHCl ₃ , <i>i</i> -Pr ₃ P	JCS Perkin I 1921 (1993)



TL 29 6253 (1988)

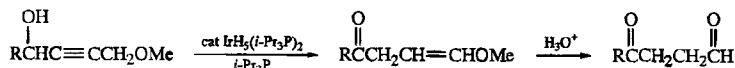
Catalyst

IrH ₅ (<i>i</i> -Pr ₃ P) ₂	JCS Perkin I 1921 (1993)
Pd ₂ (DBA) ₃ ·CHCl ₃ , <i>n</i> -Bu ₃ P	JOC 56 5774 (1991) JCS Perkin I 1921 (1993)

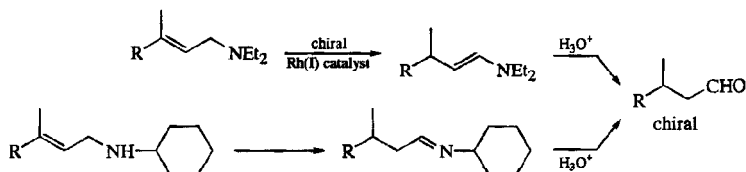


X, R = OR, aryl; OR, vinylic; aryl, aryl

TL 29 1457 (1988)

*n*-Bu₃N TL 29 1457 (1988) (R = aryl, vinylic)cat ClRh(PPh₃)₃, cat *n*-Bu₃P TL 36 4497 (1995)

JOC 56 6712 (1991)



JACS 106 5208 (1984)

Pure Appl Chem 57 1845 (1985)

2. Epoxides



Reviews:

Chem Rev 59 737 (1959)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 3, Part 3.3, p 733

electrogenerated H⁺

TL 24 2857 (1983)

JOC 50 3160 (1985)

LiClO₄, benzene

TL 29 2575 (1988)

LiClO₄ or LiBr, *n*-Bu₃PO

JACS 90 4193 (1968)

LiBr-HMPA, benzene

JACS 93 1693 (1971)

JOC 53 227 (1988)

LiI

CC 1200 (1982)

Org Syn Coll Vol 6 320 (1988)

TL 31 6609 (1990)

NaI, CH₃I, DMF

Acta Chem Scand 18 1551 (1964)

NaI, *n*-PrI, DMSO

CC 227 (1968)

MgBr₂

Helv 31 1077 (1948)

JACS 76 4402 (1954); 79 6283 (1957)

TL 23 4389 (1982)

BeCl₂/AgBF₄

TL 23 4385 (1982)

BF₃·OEt₂

JACS 76 1235 (1954); 84 867 (1962); 92 2574

(1970); 105 7352 (1983); 108 3443, 4586 (1986);

112 6690 (1990); 117 5245 (1995)

Org Syn Coll Vol 4 375 (1963)

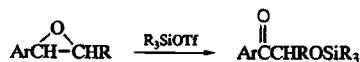
Austral J Chem 30 1137 (1977); 36 97 (1983)

TL 23 4389 (1982); 29 1263, 2575 (1988)

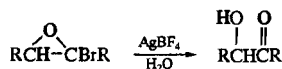
JOC 53 3195 (1988); 54 2125 (1989)

SL 491 (1991)

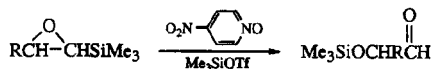
$B(C_6F_5)_3$	SL 721 (1995)
$AlCl_3$	JACS 80 1744 (1958)
MABR	TL 30 5607 (1989); 35 711 (1994) JACS 113 5449 (1991) (chiral) SL 363, 491, 579, 857 (1991)
$SnCl_4$	SL 895 (1993)
SbF_5	SL 491 (1991)
$(Ph_3C)SbCl_6$	TL 30 3097 (1989)
$(p\text{-}BrC_6H_4)_3N^+ SbCl_6^-$	TL 30 3097 (1989)
cat $RuCl_3$	JOC 57 5523 (1992)
cat $Co_2(CO)_8$	JOC 27 2706 (1962)
cat $ClRh(PPh_3)_3$	JOC 42 2299 (1977)
$NiBr_2(PPh_3)_2$	CL 1323 (1986)
cat $Pd(OAc)_2$, cat $n\text{-}Bu_3P$ or Ph_3P	JOC 59 7195 (1994)
$ZnBr_2$	JOC 30 4271 (1965)



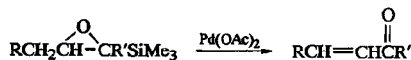
TL 35 8299 (1994)



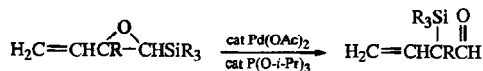
TL 36 6519 (1995)



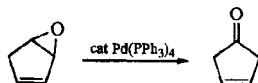
TL 35 3387 (1994)



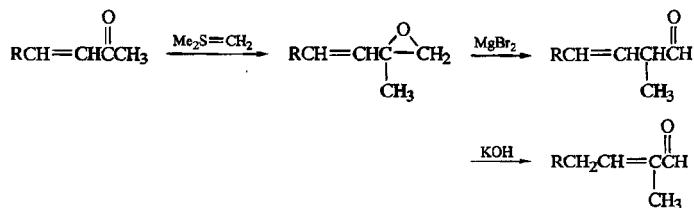
CL 1997 (1982)



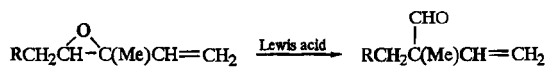
TL 33 3859 (1992)



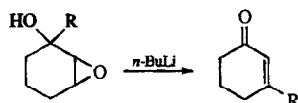
JACS 101 1623 (1979)



Helv 63 1665 (1980)



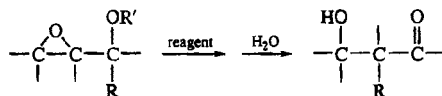
JACS 117 7379 (1995)



JACS 117 12700 (1995)



JACS 115 12208 (1993)



R'

Reagent

H

BF₃·OEt₂

JACS 108 3827 (1986)

TL 27 6233, 6237 (1986); 28 5891 (1987)

CL 113 (1987)

JOC 58 5944 (1993)

SnCl₄SiMe₃BF₃·OEt₂

TL 28 5891 (1987); 30 5443 (1989)

Tetr 44 4061 (1988)

TL 28 3515 (1987)

Tetr 44 4061 (1988)

JACS 108 3827 (1986)

TL 31 3335 (1990)

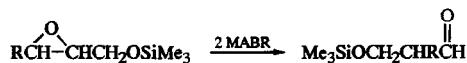
TL 30 5443 (1989)

TL 27 6233, 6237 (1986); 28 5891 (1987)

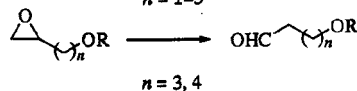
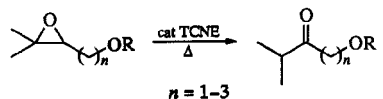
Tetr 44 4061 (1988)

TL 28 3515 (1987)

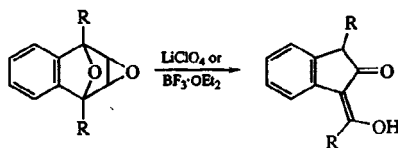
cat Me₃SiX (X = I, OTf)TiCl₄*i*-PrOTfCl₃*(i*-PrO)₂TiCl₂cat Me₃SiX (X = I, OTf)



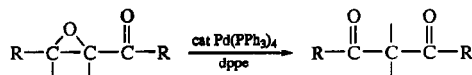
JACS 111 6431 (1989)



CC. 17 (1993)



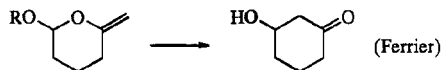
TL 32 851 (1991)



JACS 102 2095 (1980)

3. Vinylic Ethers

See also page 000, Section 000.

HgCl₂, H₂O

JCS Perkin I 1455 (1979)
 Agric Biol Chem 45 301 (1981)
 Syn 710 (1983)
 Ann 551 (1986)
 TL 28 2871 (1987); 36 195 (1995)
 Carbohydr Res 175 227 (1988)
 JOC 59 3135 (1994); 60 3280 (1995)

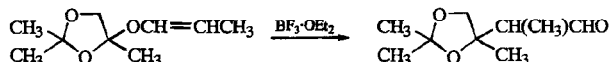
HgSO₄, H₂O

CC 330 (1985)
 Carbohydr Res 135 231 (1985)
 Compt Rend II 301 1345 (1985)

HgSO₄, H₂O, H₂SO₄

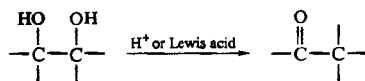
JOC 54 3764 (1989)

$\text{Hg}(\text{OAc})_2, \text{H}_2\text{O}$	CC 944 (1980); 1008 (1987) JCS Perkin I 2413 (1985) Ann 551 (1986) JACS 113 9885 (1991)
$\text{Hg}(\text{OAc})_2, \text{H}_2\text{O}, \text{HOAc}$	SL 969 (1992)
$\text{Hg}(\text{O}_2\text{CCF}_3)_2, \text{H}_2\text{O}$	CC 1268 (1984) JOC 56 2976 (1991); 58 4441 (1993); 60 6103 (1995) JACS 113 9883 (1991) TL 32 4525 (1991)
cat PdX_2 ($\text{X} = \text{Cl}, \text{OAc}$), $\text{H}_2\text{O}, \text{H}_2\text{SO}_4$	TL 29 6589 (1988)



JOC 53 1860 (1988)

4. Pinacol and Related Rearrangements



Reviews and leading references:

Org Syn Coll Vol 1 462 (1941)

Quart Rev 14 357 (1960)

"Molecular Rearrangements," Interscience, New York (1963), Vol 1, Chpt 1

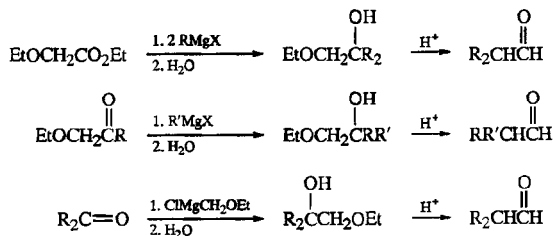
JOC 28 2690 (1963); 58 5546 (1993); 59 468 (1994)

"Supplement E: The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues," Ed. S. Patai, J. Wiley & Sons, New York (1980), Part 2, p 722

TL 30 945 (1989) (microwave irradiation on montmorillonite); 34 7837 (1993) (cat NOBF_4 or electrolysis); 36 1055 (1995)

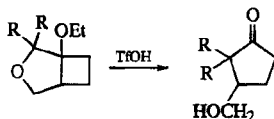
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 3.2, p 721

J Chem Ed 69 667 (1992)

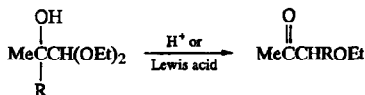


JACS 61 2134 (1939); 68 2339 (1946)

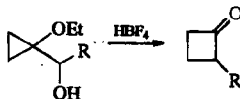
BSCF 459 (1959)



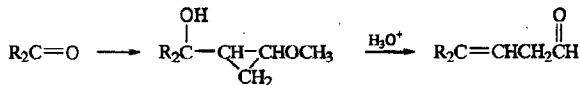
JOC 60 2526 (1995)



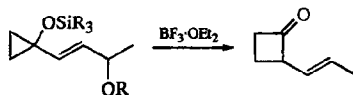
TL 35 5027 (1994)



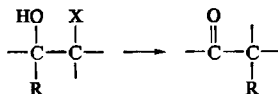
Org Syn Coll Vol 8 556 (1993)



TL 3685 (1975)



TL 37 4135 (1990)



X = Cl, OTs

JACS 83 1251 (1961)

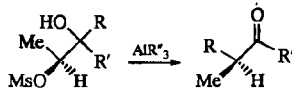
CC 565 (1968)

TL 5553 (1968)

JOC 33 453 (1968); 37 4090 (1972); 55 1589 (1990); 58 4572 (1993)

JCS Perkin I 225 (1987)

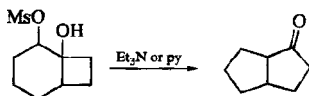
See also page 1562, Section 3.3.



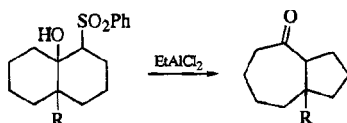
R = aryl, vinylic, cyclopropyl

TL 24 4997 (1983); 25 1817 (1984); 30 5443 (1989)

SL 129 (1992)



JOC 58 4572 (1993)



JACS 114 5432 (1992)

Br₂/AgNO₃, H₂O, MeOH

JOC 59 468 (1994)

(CF₃CO)₂O, H₂O₂, BF₃·OEt₂

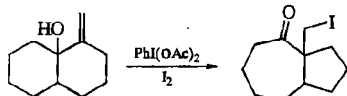
JOC 59 468 (1994)

Hg(OAc)₂, H₂O/NaBH₄

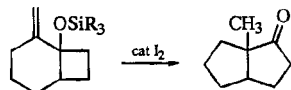
JOC 59 468 (1994)

5. Ring Rearrangement

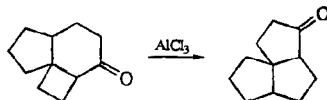
See also page 1281, Section 4.



TL 32 1591 (1991)

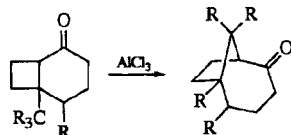


SL 263 (1990)

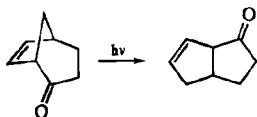


JACS 111 3707 (1989)

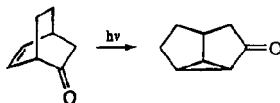
JOC 56 463 (1991)



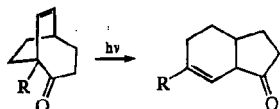
JOC 56 6742 (1991)



JOC 58 4756 (1993)



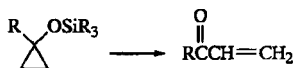
Angew Int 21 820 (1982) (review)



JOC 53 3669 (1988)

6. Ring Opening

See also page 1230, Section 13.

TeCl₄/DMSO

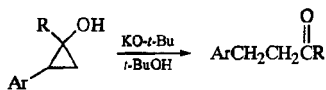
TL 32 229 (1991)

SnCl₄ or RSnCl₃/base

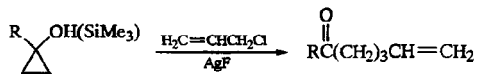
JOC 57 17 (1992)

Hg(OAc)₂/PdCl₂, LiCl, Li₂CO₃

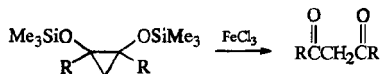
TL 21 4283 (1980)



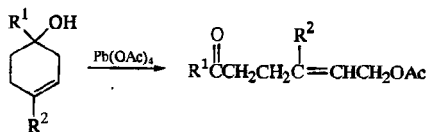
JOC 57 5561 (1992)



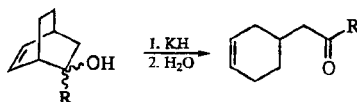
TL 29 6137 (1988)



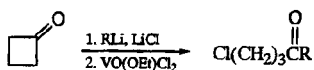
JOC 59 5700 (1994)



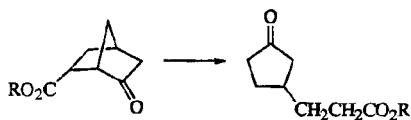
TL 29 2119 (1988)



Helv 64 2193 (1981)



JOC 56 2264 (1991)

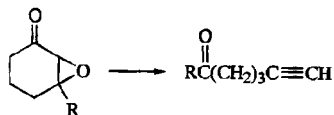
Li, NH₃

TL 31 4899 (1990)

JOC 58 1483 (1993)

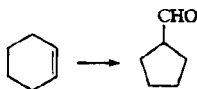
Li, naphthalene

JOC 58 1483 (1993)



See page 569, Section 2.

7. Ring Contraction

Hg(ClO₄)₂, H₂O

JACS 95 2591 (1973)

Tl(ClO₄)₃, H₂O

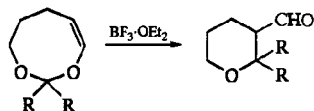
JACS 95 2591 (1973)

Ti(NO₃)₃, CH₃OH/H₃O⁺TL 5275 (1970); 4753 (1971); 29 1841 (1988)
(glycal)

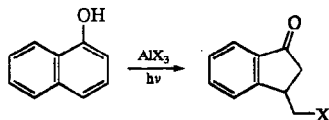
JACS 95 3635 (1973)

PhSeCl/H₂O, Et₃N/*m*-ClC₆H₄CO₂H

TL 29 2711 (1988) (glycal)

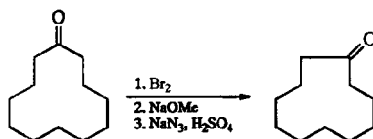


TL 31 649 (1990)

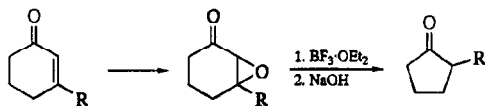


X = Cl, Br

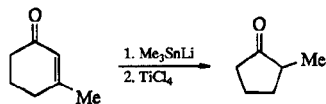
JOC 56 5745 (1991)



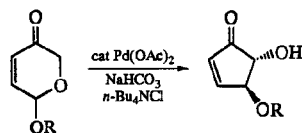
Org Syn Coll Vol 6 368 (1988)



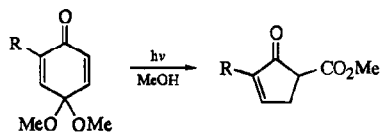
TL 31 4761 (1990)



JOC 53 1894 (1988)



TL 30 4489 (1989)



TL 33 2155 (1992)

8. Ring Expansion

See page 1467, Section 12 for related reactions.

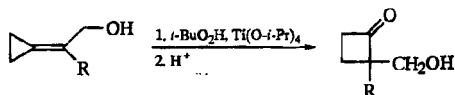
Reviews

"Carbocyclic Ring Expansion Reactions," Academic Press, New York (1968)

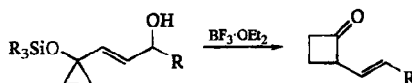
M. Hesse, "Ring Enlargement in Organic Chemistry," VCH, Weinheim (1991)

Tetr 49 10749 (1993)

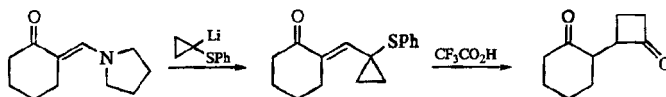
Chem Rev 93 2091 (1993) (free radical)



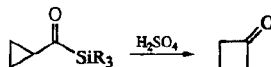
IOC 57 1707 (1992); 59 74 (1994) (chiral); 60 6785 (1995)



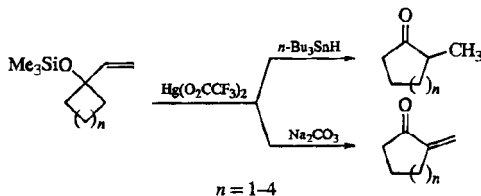
TL 29 1537 (1988)



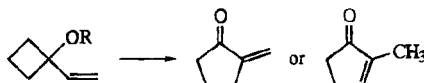
IOC 54 4698 (1989)



TL 36 1667 (1995)



TL 33 4325 (1992)



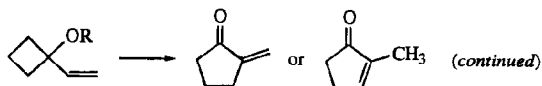
Reagent(s)

cat PdCl₂(PhCN)₂, benzoquinone

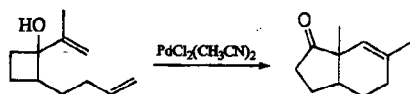
TL 26 2503 (1985)

R

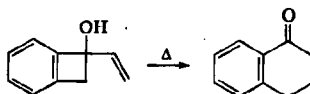
H

RSiR₃Reagent(s)

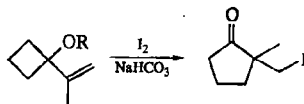
cat PdCl ₂ (PhCN) ₂ , benzoquinone	Helv 71 1392 (1988)
PdCl ₂ (PhCN) ₂	JCS Perkin I 177 (1990)
cat PdCl ₂ (CH ₃ CN) ₂ , benzoquinone	JCS Perkin I 2329 (1993)
PdCl ₂ (CH ₃ CN) ₂	JOC 59 74 (1993)
Pd(OAc) ₂ , AsPh ₃	JOC 59 74 (1993)



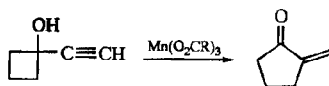
SL 599 (1994)



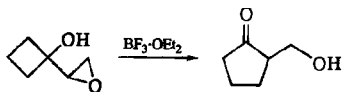
TL 32 819 (1991)

R = H, SiR₃

TL 36 8799 (1995)



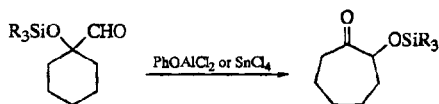
JOC 58 7228 (1993); 59 5419 (1994)



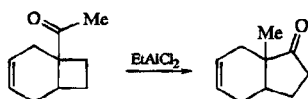
JCS Perkin I 2329 (1993)



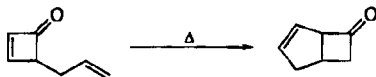
TL 29 1815 (1988)



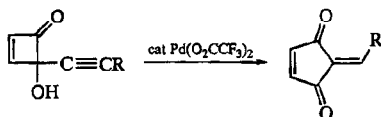
TL 30 4267 (1989)



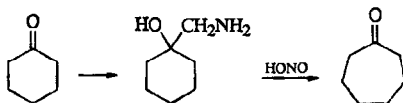
TL 33 2583 (1992)



JOC 54 6018 (1989)



JACS 109 7908 (1987)



Org Rxs 11 157 (1960) (review)

Org Syn Coll Vol 4 221 (1963)

JCS 2513 (1965)

"Carbocyclic Ring Expansion Reactions," Academic Press, New York (1968), p 74 (review)

JOC 33 2069 (1968); 39 914 (1974); 43 1050 (1978); 45 185 (1980); 47 2685 (1982); 52 2602 (1987); 58 4756 (1993)

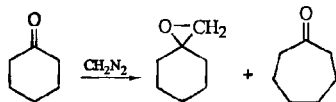
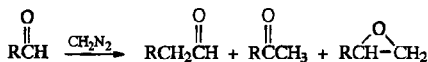
Angew Int 10 491 (1971)

Tetr 29 1941 (1973)

TL 4929 (1973)

Can J Chem 57 1557 (1979)

JACS 116 2759 (1994)



Newer Methods Prep Org Chem 1 513 (1948) (review)

Org Rxs 8 364 (1954) (review)

JACS 82 4099 (1960); 84 989 (1962) (2-alken-1-one to 3-alken-1-one)

Org Syn Coll Vol 4 225 (1963)

Can J Chem 46 1913 (1968); 57 1557 (1979)

"Carbocyclic Ring Expansion Reactions," Academic Press, New York (1968), Chpt 4 (review)

JOC 33 4090 (1968); 53 5168 (1988); 59 2114 (1994)

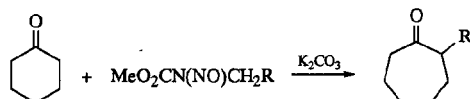
TL 393 (1971); 32 1637 (1991); 36 1171 (1995)

Tetr 29 1941 (1973)

JCS Perkin I 477 (1982)

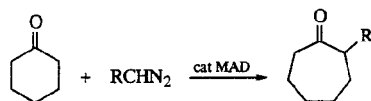
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 1, Part 3.3, p 843 (review)

SL 357 (1992)

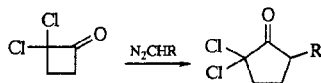


J Prakt Chem 34 272 (1966)

JOC 54 4702 (1989)



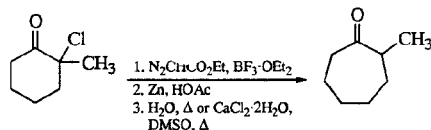
JOC 59 4725 (1994)



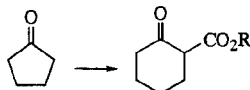
JACS 101 4003 (1979); 105 2435 (1983)

JOC 45 2036 (1980); 48 4763 (1983); 50 3957 (1985); 56 7048 (1991); 59 1199 (1994)

TL 30 7065 (1989)



JOC 48 2590 (1983)



$\text{N}_2\text{CHCO}_2\text{R, (Et}_3\text{O)BF}_4$

JACS 92 5767 (1970); 115 3816 (1993)

JOC 42 459, 466 (1977)

Can J Chem 57 1557 (1979)

N_2CHCO_2R , $BF_3 \cdot OEt_2$

Can J Chem 42 1333 (1964)

TL 4937 (1973)

Syn Commun 5 125 (1975); 8 413 (1978)

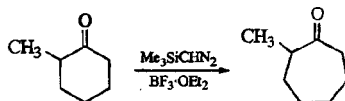
JOC 52 3455 (1987); 54 187, 5086 (1989); 55 3493, 3498 (1990)

 N_2CHCO_2R , $SbCl_5$

JOC 42 459 (1977); 50 3957 (1985)

 N_2CHCO_2R , base/ Δ , hv, H^+ or transition metal catalyst

See page 1311, Section 10.

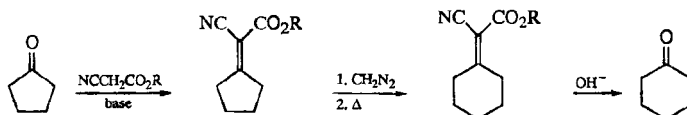


TL 21 4619 (1980)

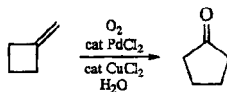
Chem Pharm Bull 30 119 (1982)



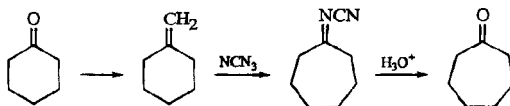
JACS 117 12015 (1995)



J Chem Res (S) 436 (1978)



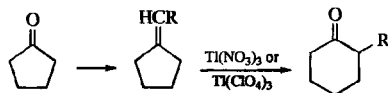
CC 583 (1977)



JACS 86 4506 (1964); 91 3676 (1969) (diene)

JOC 38 2821 (1973)

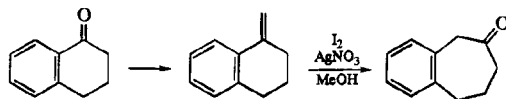
TL 28 3209 (1987)



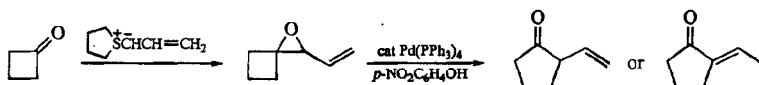
JACS 95 2591 (1973)

JOC 38 3455 (1973)

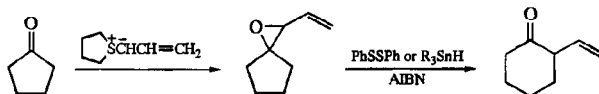
TL 1827 (1977)



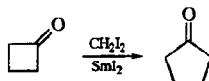
TL 27 3783 (1986)



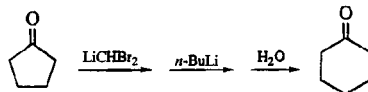
TL 32 3395 (1991)



TL 32 6575 (1991)



TL 36 1995 (1995)



JOMC 40 C1 (1972); 97 325 (1975)

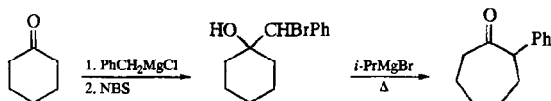
Compt Rend 276 433 (1973)

JACS 96 6510 (1974); 106 3030 (1984)

TL 2617 (1976); 28 585 (1987); 36 3965 (1995)

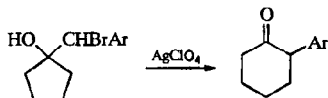
BCSJ 50 1592 (1977)

JOC 57 1926 (1992)

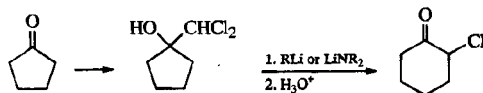


TL 5327 (1967)

JOC 33 453 (1968)

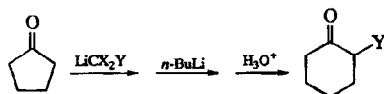


TL 33 5117 (1992)



Ber 106 2626 (1973)

BCSJ 50 1592 (1977)

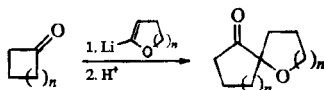


X = Cl, Br; Y = Cl, alkyl, aryl

JOMC 40 C1 (1972); 97 325 (1975)

Compt Rend C 276 433 (1973)

Syn 968 (1979)

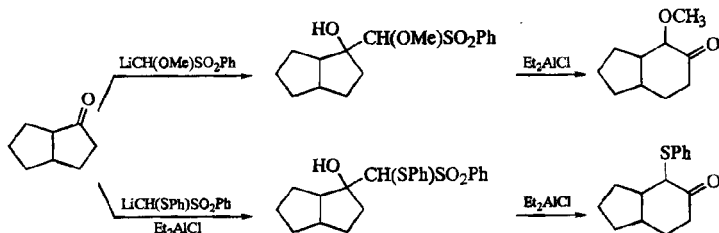
 $n = 1, 2$

Heterocycles 30 765 (1990)

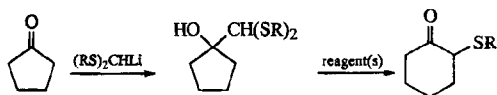
JACS 113 5073 (1991)

JOC 57 3947 (1992)

TL 34 8019 (1993)



JACS 109 4124 (1987)

Reagent(s)

CuOTf

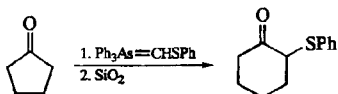
JACS 97 4749 (1975); 107 4339 (1985)

Cu(OTf)₂·PhH, *i*-Pr₂NEt

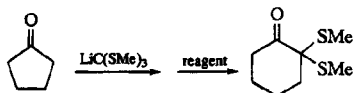
JACS 115 2992 (1993)

2 RLi/H₂O

TL 28 2203 (1987)



JACS 115 11606 (1993)

Reagent

HCl

TL 29 1493 (1988)

HgCl₂

TL 21 4301 (1980)

CuBr·SMe₂

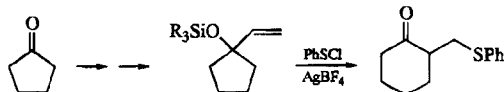
TL 35 6041 (1994)

CuBF₄·4CH₃CN

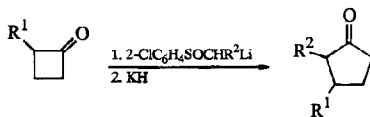
JOC 49 608 (1984)

CuClO₄·4CH₃CN

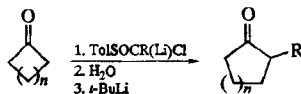
JOC 49 608 (1984); 50 1573 (1985)



TL 30 6181 (1989)

R¹ = aryl, vinylic

JOC 52 774 (1987)

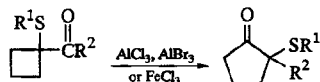
 $n = 1-3, 5, 9$

TL 33 7543 (1992)

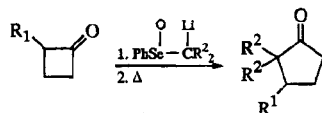


$n = 1-4, 7, 9$

TL 33 7181 (1992)

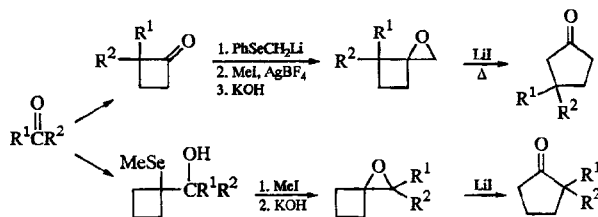


TL 24 79 (1983)

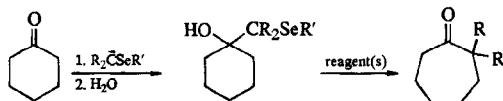


$R^1 = \text{alkyl}$

JOC 48 2098 (1983); 52 774 (1987)



CC 1200 (1982)



Reagent(s)

KOH, $(\text{PhCH}_2\text{NEt}_3)\text{Cl}$, CH_2Cl_2

TL 28 1545, 1549 (1987)

TiOEt , HCCl_3

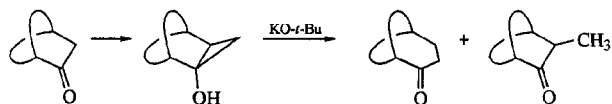
TL 23 4385 (1982); 25 2713, 5043 (1984); 28 1545, 1549 (1987); 30 575 (1989)
JOC 50 5200 (1985) (enones)
CC 702 (1986)

AgBF_4

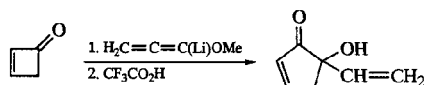
TL 23 983, 4385 (1982); 28 1545 (1987); 30 575 (1989)

MeOSO_3F

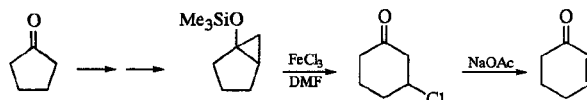
TL 23 4385 (1982)
CC 564 (1982)



Can J Chem 58 2730 (1980)



JOC 55 4614 (1990)

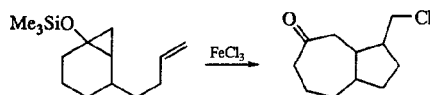


JOC 41 2073 (1976); 44 4481 (1979); 51 3405 (1986)

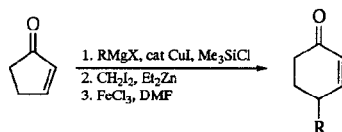
Org Syn 59 113 (1980)

Org Syn Coll Vol 6 327 (1988)

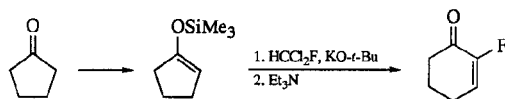
SL 357, 969 (1992)



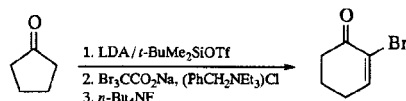
SL 809 (1992); 592 (1993)



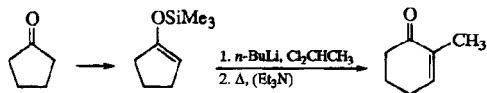
TL 34 7291 (1993)



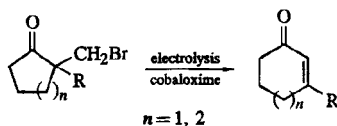
BSCF 455 (1985)



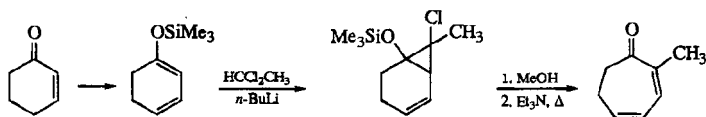
TL 34 7295 (1993)



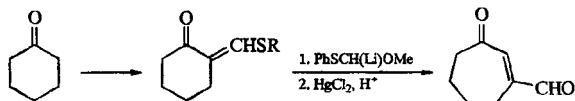
Syn 289, 291 (1981)
JACS 109 3025 (1987)



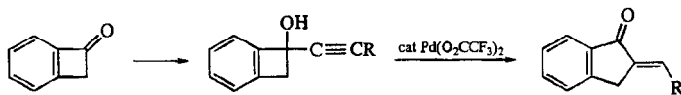
JOC 56 5945 (1991)



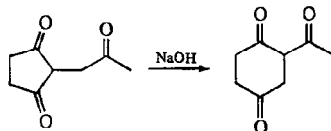
TL 22 645 (1981)



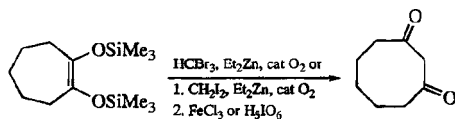
TL 31 1873 (1990)



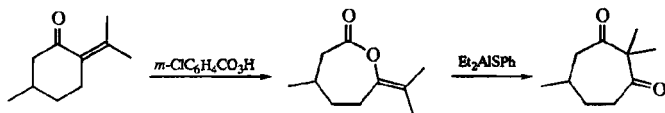
JACS 109 7908 (1987); 112 291 (1990)
Pure Appl Chem 60 27 (1988)



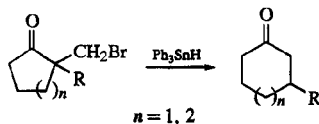
TL 34 4759 (1993)



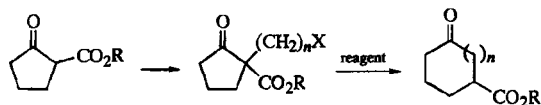
JOC 52 3603 (1987)



TL 23 99 (1982)

 $n = 1, 2$

IOC 56 5945 (1991)



Reagent

 n n -Bu₃SnH

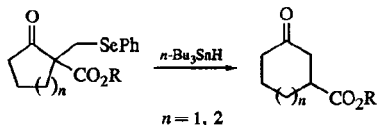
1, 3, 4

JCS Perkin I 1139 (1986)
 JACS 109 3493, 6548 (1987);
 110 2565 (1988)
 CC 666 (1987)
 TL 30 6129 (1989); 32 565
 (1991); 34 7709 (1993)

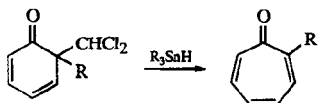
electrolysis

1, 3

IOC 55 5037 (1990)

 $n = 1, 2$

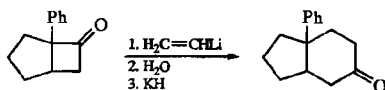
TL 30 6129 (1989)



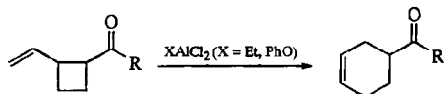
CC 743 (1984)

Tetr 43 5031 (1987)

SL 363 (1994)



TL 29 3175 (1988)



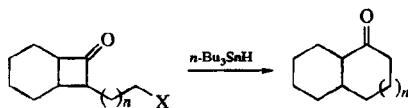
TL 31 6027 (1990)



X = Br, I; n = 1, 2

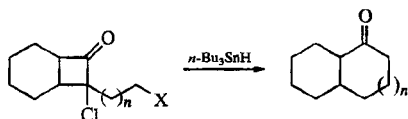
JACS 113 9875 (1991)

TL 36 2729 (1995)



X = Br, I; n = 2, 3

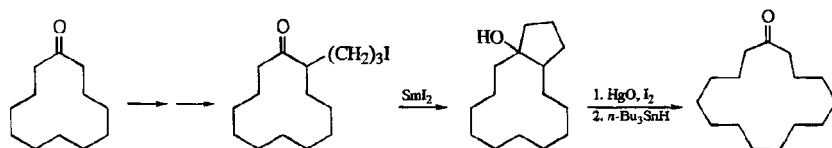
JOC 57 7163 (1992)



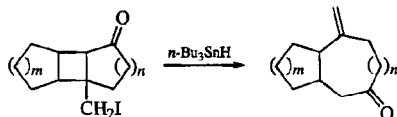
X = Br, I; n = 1-3

JOC 57 7163 (1992)

TL 35 3865, 5563 (1994)

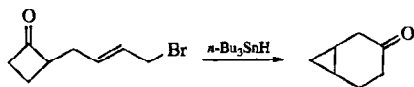


TL 28 3963 (1987)

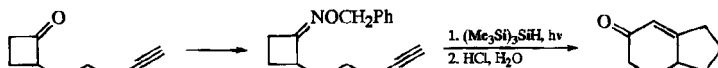


m, n = 1, 1; 1, 2; 2, 1; 2, 2

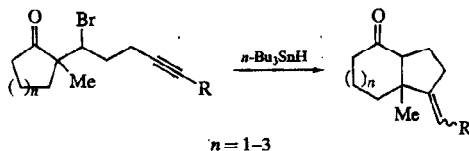
JOC 60 2183 (1995)



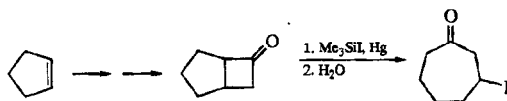
TL 33 7307 (1992)



TL 34 6787 (1993)

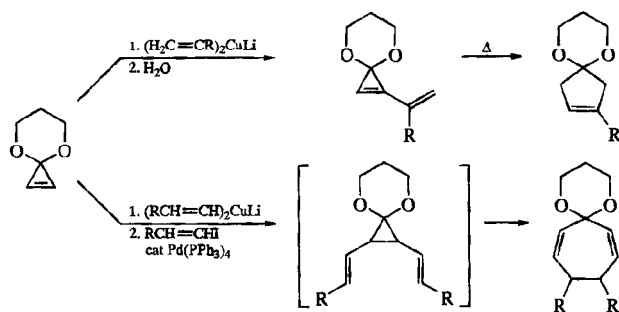


JOC 55 5442 (1990); 57 1429 (1992)

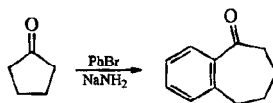


TL 21 2639 (1980)

JACS 114 10084 (1992)

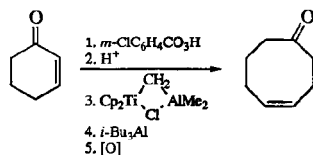


JACS 110 1297 (1988)

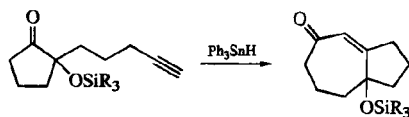


BSCF 302 (1971); 3493 (1973)

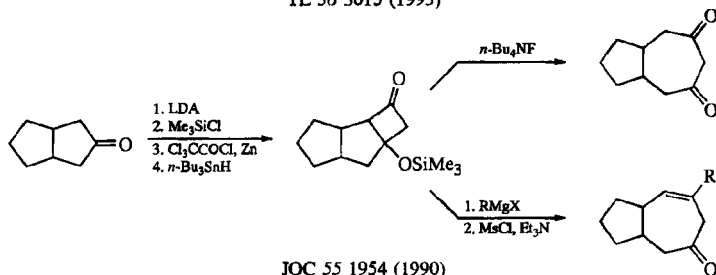
JACS 116 9471 (1994)



JACS 113 2763 (1991)

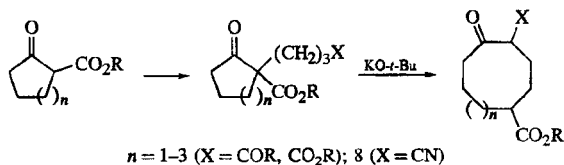


TL 36 3015 (1995)

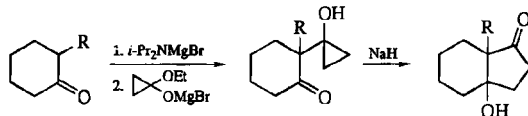


JOC 55 1954 (1990)

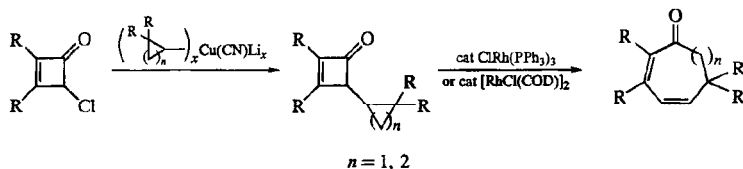
TL 32 6011 (1991)



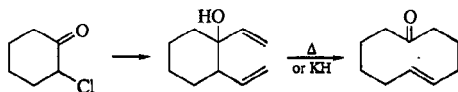
JOC 55 820 (1990)



TL 29 1243 (1988)



JACS 115 4895 (1993)



TL 509 (1970)

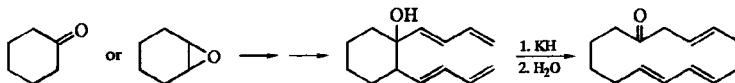
CL 667 (1973)

JACS 101 2493 (1979); 105 625 (1983)

BCSJ 53 2958 (1980); 58 146 (1985)

JOC 51 1124 (1986)

See page 1306, Section 9.10.



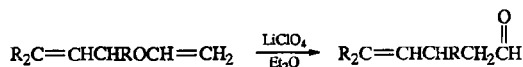
TL 22 2471 (1981)

Tetr 37 3967 (1981)

JACS 107 7771 (1985)

9. Electrocyclic Rearrangements

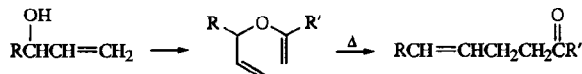
9.1. 1,3-Claisen



JACS 113 5488 (1991)

TL 34 5001 (1993)

9.2. 3,3-Claisen



Reviews:

Chem Rev 27 495 (1940); 84 205 (1984) (catalysis); 88 1423 (1988)

Org Rxs 2 1 (1944); 22 1 (1975)

Quart Rev 22 391 (1968)

Chem in Britain 5 111 (1969)

Acct Chem Res 10 227 (1977)

Syn 589 (1977)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 7.2, p 827

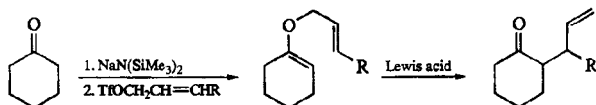
Key articles and recent references:

JACS 81 3379 (1959); 83 198 (1961); 89 4559 (1967); 92 3126 (1970); 93 5805, 5813 (1971); 103 6983, 6984 (1981); 104 4972 (1982) (carbanion acceleration); 106 6868 (1984); 107 2730, 7352

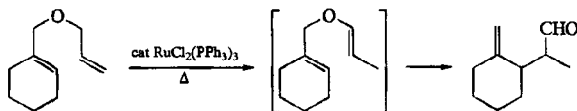
(1985); 109 1160 (alkoxy substitution), 1170 (substituent effects), 3987 (1987); 110 7922 (1988) (organoaluminum stereoselectivity); 111 8263, 8878 (carbanion acceleration) (1989); 112 316 (organoaluminum stereoselectivity), 7791 (chiral, organoaluminum) (1990); 113 2762 (1991); 114 2635 (1992); 116 10948 (1994); 117 1165 (1995) (chiral, organoaluminum)
 TL 493 (1961); 2145, 3243, 3253 (1969); 22 3985 (1981) (organoaluminum promotion); 23 3143 (1982); 24 3, 4397 (1983); 25 1543, 4579 (1984); 26 3655 (1985); 27 6267 (PdCl₂ catalyzed), 6311 (1986); 28 3065, 5879 (catalyst diastereoselectivity) (1987); 29 1669 (1988); 30 1265 (regioselective organoaluminum promotion), 2469 (carbanion acceleration) (1989); 31 4041, 4147 (chiral, acceleration by water), 6799 (1990); 33 6477 (1992); 34 1721 (1993); 35 2907, 4853 (1994); 36 6647 (1995)
 Helv 50 2091, 2095 (1967); 61 3075 (1978)
 CC 264 (1969)
 Org Syn Coll Vol 5 25 (1973); 6 298 (1988); 8 536 (1993)
 JOC 48 1829, 3876 (1983); 49 2347 (1984); 52 5190, 5742 (carbanion acceleration) (1987); 53 4992, 5885 (1988); 54 515, 4278, 5849 (acceleration by water) (1989); 55 1703, 1813, 5671 (1990); 56 1003, 5063 (1991) (both anion acceleration); 58 62 (1993); 59 3270, 3427 (1994); 60 6289 (1995)
 Tetr 42 2911 (1986)
 SL 793 (1991) (chiral organoalane); 447 (1995)

Heteroatom systems:

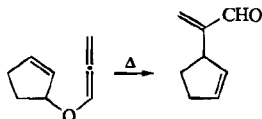
Fortschr Chem Forsch 16 75 (1970)



TL 36 803 (1995)

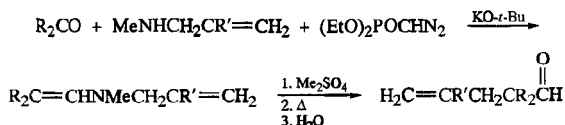


JOC 42 3360 (1977); 59 6038 (1994)

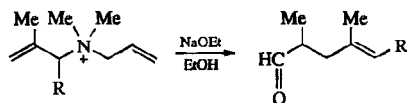


JOC 58 5702 (1993)

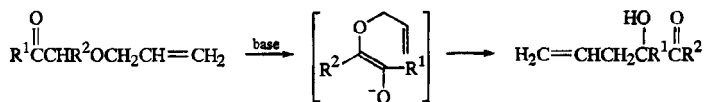
9.3. Amino-Claisen



TL 25 2303 (1984)



SL 739 (1994)

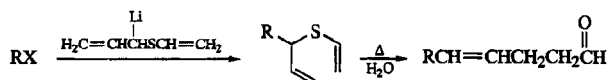
9.4. Oxy-Claisen

JACS 107 5572 (1985)

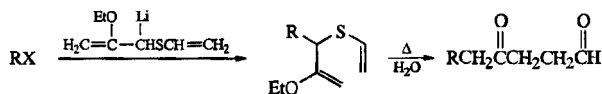
TL 29 4229 (1988)

9.5. Thio-Claisen

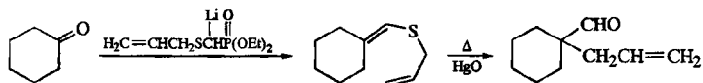
Review: Phosphorus and Sulfur 7 69 (1979)



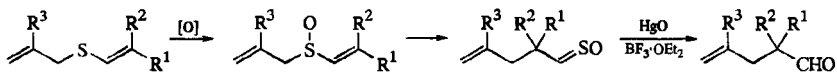
JACS 95 2693 (1973)



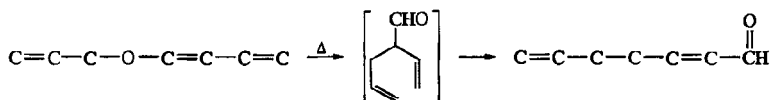
JACS 95 4446 (1973)



JACS 92 5522 (1970)

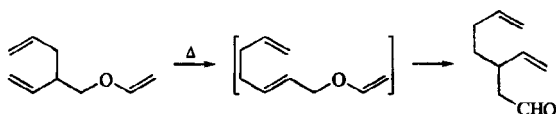


JACS 107 6731 (1985)

9.6. Claisen-Cope

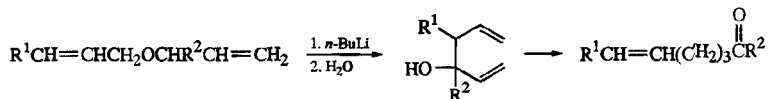
CC 947 (1967); 1657 (1968); 248 (1972)
 JACS 91 3281 (1969)
 Helv 53 1145 (1970)
 JCS C 220 (1970)
 JCS Perkin I 2634, 2741 (1973)
 TL 23 3839 (1982)

9.7. Cope-Claisen

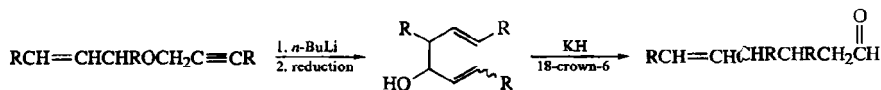


JACS 101 1611 (1979); 102 880, 6576 (1980); 103 1853 (1981); 104 7181 (1982)
 JOC 47 5229 (1982); 49 3278 (1984)

9.8. 2,3-Wittig-oxy-Cope

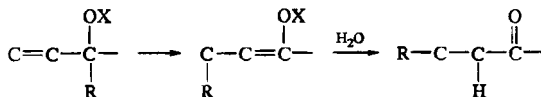


CL 1349, 1643 (1982)
 TL 23 3931 (1982); 35 7077 (1994)
 Tetr 42 2911 (1986)
 CC 1469 (1994)



JOC 56 5973 (1991)

9.9. 1,3-Oxy-Cope



R

benzylic

X

K

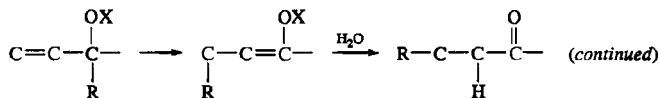
SiMe₃

allylic

H

CC 846 (1976)
 JOC 43 1050 (1978); 45 185 (1980); 47
 798 (1982)
 JACS 103 7661 (1981); 104 4411 (1982)
 CC 846 (1976)
 JOC 47 798 (1982)

JACS 86 5017, 5019 (1964); 94 7074 (1972);
 104 4411 (1982)

RX

K

CC 846 (1976)

JOC 43 1050 (1978); 52 3798 (1987)

JACS 104 891 (1982)

TL 30 3833 (1989)

SiMe₃

JACS 94 7074 (1972); 96 200 (1974)

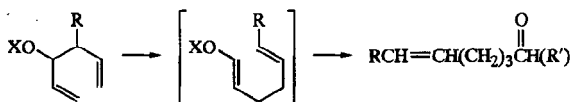
CC 846 (1976)

JOC 41 1233 (1976); 42 280 (1977); 52 3798 (1987)



K

JOC 43 4903 (1978)

9.10. 3,3-Oxy-Cope

Reviews:

SL 67 (1990)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 7.1, p 785

X

H

JACS 86 5017, 5019 (1964); 87 1150 (1965); 89 3462 (1967); 90 4729, 4730, 4732, 6141 (1-alken-5-yn-3-ol) (1968); 92 2404 (1970) (5-alken-1-yn-3-ol); 94 4779, 7074 (1972); 95 5281 (1973); 102 3972 (1980); 106 3869 (1984) (5-alken-1-yn-3-ol); 108 6343 (1986); 111 1815 (1989)

TL 6115 (1966); 1337, 1341, 2681 (1969); 509 (1970); 23 4263 (1982) [Hg(O₂CCF₃)₂ promoted]; 30 2525 (1989); 32 319 (1991); 35 2761 (1994)

CC 143 (1968) (1-alken-5-yn-3-ol); 491 (1974)

BSCF 1491 (1968)

JOC 35 856 (1970); 46 5447 (1981); 47 4815 (1982); 53 2214 (1988) (5-alken-1-yn-3-ol); 54 4278 (1989); 57 4512 (1992)

CL 667 (1973)

BCSJ 53 2958 (1980)

alkali metal

JACS 97 4765 (1975); 99 4186 (1977); 100 2242, 4309 (1978); 101 2493 (1979); 102 774, 2463, 3972 (1980); 103 6235 (1981); 105 625 (1983); 106 4038, 7614 (1984); 108 7873 (1986); 110 890 (1988); 111 1815 (1989); 112 260, 265, 277, 5562, 8478, 9284 (1990); 113 967, 1335 (1991); 114 5018, 6910 (1992); 117 8486 (1995)

Angew Int 15 437 (1976); 29 609 (1990) (review)

Ber 112 1420 (1979)

JOC 46 9, 2199, 4272, 5447 (1981); 47 2268, 3190 (1982); 50 5747 (1985); 51 1124 (1986); 52 3798 (1987); 54 997, 2278, 2291, 4083, 4576, 5205 (1989); 55 324, 3597, 5426 (1990); 56 321, 912, 6538 (1991); 57 4103, 7118 (1992); 58 661, 2349, 3557, 3912, 4245, 4254, 4262, 4952, 5482 (1,2,6-alkatrien-4-one), 6874 (1993); 59 885, 1444, 2033 (1994); 60 889, 897, 7849, 7857 (1995)

TL 22 3167, 4651 (1981); 24 2931 (1983); 25 5103 (1984); 28 31, 5351 (1987); 29 273 (1988); 30 2525, 4045, 4427 (1989); 31 4547 (1990); 33 923 (1992); 34 8395 (1993); 35 7077, 9025 (1994); 36 673 (1995)

Tetr 38 2195 (1982); 49 1025 (1993)

J Ind Chem Soc 61 99 (1984) (review)

BCSJ 58 146 (1985)

SL 663, 729 (1990)

Org Rxs 43 93 (1993) (review)

SiR₃

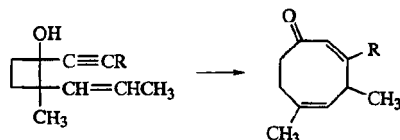
JACS 94 7074 (1972); 95 5281 (1973); 96 200 (1974); 111 1815 (1989); 117 9919 (1995)

JOC 41 1233 (1976); 46 5447 (1981); 52 622, 3798 (1987)

R

JOC 46 5447 (1981)

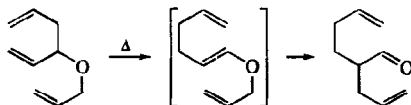
JACS 117 9919 (1995)



JACS 106 3869 (1984)

JOC 53 2214 (1988)

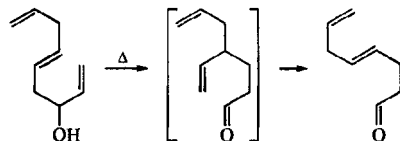
9.11. Oxy-Cope-Claisen



JOC 46 5448 (1981)

Tetr 42 2911 (1986)

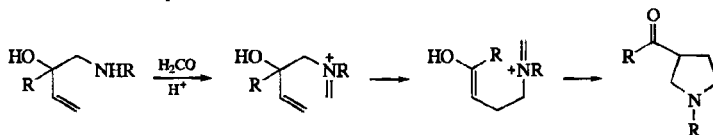
9.12. Oxy-Cope-Cope



JOC 46 5448 (1981)

Tetr 42 2911 (1986)

9.13. Mannich-aza-Cope



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 4.4, p 1007

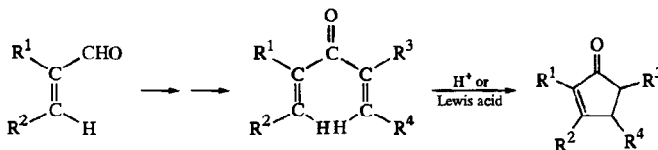
JACS 113 2598, 5085 (1991)

9.14. Carroll

See page 1528, Section 22.

9.15. Nazarov

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 6.3, p 751



JCS 1430 (1952)

J Gen Chem USSR 27 693 (1957); 30 765 (1960)

Helv 54 2913 (1971); 66 2377, 2397 (1983) (both Si-directed); 71 168 (1988)

JCS Perkin I 2271 (1972); 1026 (1973)

BCSJ 53 169 (1980)

JOC 46 3696 (1981); 54 3334 (1989); 55 5543 (1990) (Si-directed); 56 735 (1991)

JACS 104 2642 (1982) (Si-directed); 113 2610 (1991) (Si-directed)

Syn 429 (1983) (review)

TL 27 2801, 5947 (Sn-directed) (1986); 30 3531 (1989) (Si-directed); 32 2135 (Si-directed), 7731 (1991); 33

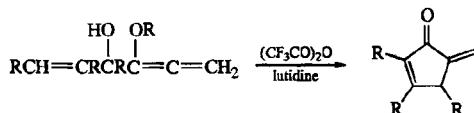
3495 (1992) (Si-directed)

Tetr 42 2821 (1986) (Si-directed); 44 4043 (1988)

SL 237 (1993); 409 (1995)

Org Rxn 45 1 (1994) (review)

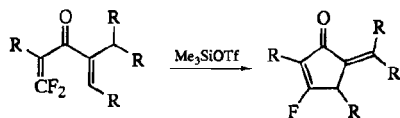
See page 1338, Section 4; and page 1345, Section 5 for related reactions.



JACS 108 3438 (1986)

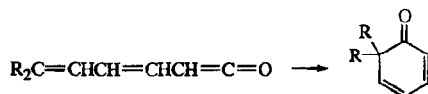
TL 30 2333 (1989)

JOC 54 46 (1989)



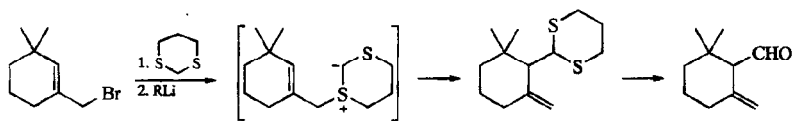
JOC 60 2320 (1995)

9.16. Electrocyclization

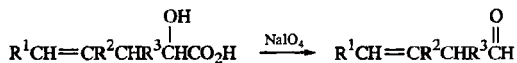
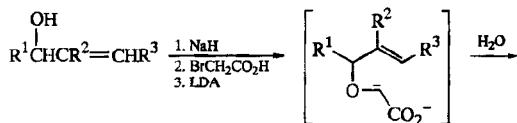


CC 1728 (1987)

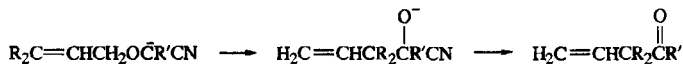
9.17. 2,3-Sigmatropic Rearrangements



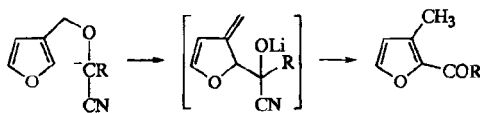
CC 757 (1972)



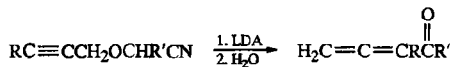
TL 22 69 (1981)



TL 24 2077 (1974)

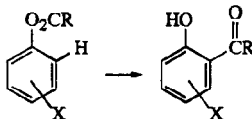


Syn Commun 7 113 (1977)



Syn Commun 7 273 (1977)

9.18. Fries Rearrangement



Review: Org Prep Proc Int 24 373 (1992)

Lewis acids:

Org Rxs 1 342 (1942) (review)

Org Syn Coll Vol 3 280 (1955)

Ind Eng Chem 47 1926 (1955)

"Friedel-Crafts and Related Reactions," Ed. G. A. Olah, Interscience, New York (1964), Vol 3, Chpt 33 (review)

TL 23 3299 (1982) (*meta*-Fries); 29 1311 (1988) (*para*-Fries); 30 2281 (1989) (*para*-Fries); 31 3943 (1990); 34 7799 (1993)

Ber 115 1089 (1982) (equilibrium)

Photochemical:

Proc Chem Soc 217 (1960)

JOC 27 2293 (1962); 46 374 (1981); 51 4432 (1986); 52 3815 (1987); 55 4083 (1990); 58 4941 (1993)

Tetr 21 1015 (1965)

V. I. Sternberg, "Organic Photochemistry," Ed. O. L. Chapman, Arnold, New York (1967), Vol 1, Chpt 3 (review)

Chem Rev 67 599 (1967) (review)

Helv 51 1980 (1968)

JACS 90 7249 (1968); 92 2187 (1970); 94 2219 (1972); 96 449 (1974)

TL 3429, 5423 (1968); 2935 (1973); 30 6483 (1989); 36 1311, 1315 (1995)

BCSJ 42 1831 (1969)

Adv Photochem 8 109 (1971) (review)

CC 289 (1974)

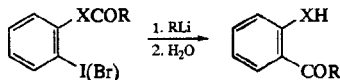
Angew Int 14 820 (1975)

BSCF 785 (1977)

Syn Commun 9 877 (1979)

Ber 113 261 (1980)

Syn 882 (1981)

 $\frac{X}{O}$

O

NR

NCO₂R

NTs

Ber 116 3375 (1983)

JOC 52 322 (1987); 55 4520 (1990)

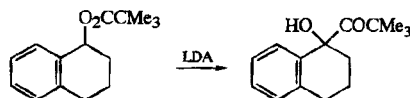
TL 35 1749 (1994)

Ber 116 3375 (1983)

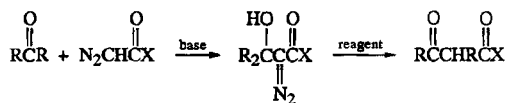
CC 1046 (1991)

CC 1046 (1991)

10. Miscellaneous Rearrangements



JOC 60 4936 (1995)

X = R, OR, NR₂Reagent Δ

IACS 94 8084 (1972)

JOC 37 2405 (1972)

 $h\nu$

JOC 37 2405 (1972)

 H_2SO_4

IACS 94 8084 (1972)

 HCl

Ann 1767 (1974)

J Chem Res (S) 76, 142 (1979)

JCS Perkin I 1822 (1977)

 $\text{BF}_3 \cdot \text{OEt}_2$

JACS 111 8231 (1989)

cat $\text{Rh}_2(\text{OAc})_4$

CC 959 (1979)

JCS Perkin I 2566 (1981)

Syn 197 (1983)

JACS 109 6187 (1987)

TL 29 4481 (1988)

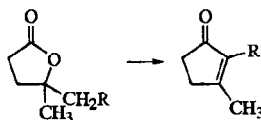
SL 111 (1995)

cat $\text{Rh}_2[\text{O}_2\text{C}(\text{CH}_2)_6\text{CH}_3]_4$

JOC 55 4144 (1990)

cat $\text{ClRh}(\text{PPh}_3)_3$, PdCl_2 or CoCl_2

Syn 197 (1983)

 P_2O_5 , MeSO_3H

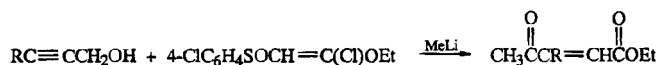
JOC 38 4071 (1973)

 P_2O_5 , H_3PO_4

JOC 54 3988 (1989)

PPA

J Ind Chem Soc 34 178 (1957)



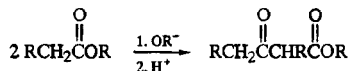
JOC 56 6987 (1991)

5. CONDENSATION REACTIONS

See also page 317, Section 3 for condensation reactions that generate a carbon-carbon double bond.

1. Acetoacetic Ester

See also page 1528, Section 22.



Org Rxs 1 266 (1942) (review)
JOC 51 268 (1986)

2. Acyloin

Reviews:

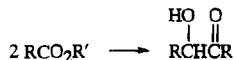
Org Rxs 4 256 (1948); 23 259 (1976)

Chem Rev 64 573 (1964)

Syn 236 (1971) (Na, Me₃SiCl)

JOC 40 393 (1975) (mechanism)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 3, Part 2.7, p 613



Na, ether

JACS 52 3988 (1930); 53 750 (1931)

Na, NH₃

JOC 5 362 (1940)

Na, xylene

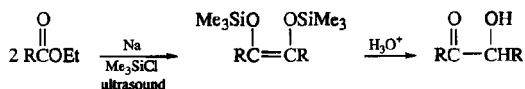
JACS 57 2303 (1935)

Org Syn Coll Vol 2 114 (1943)

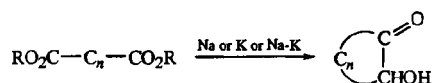
JCS C 2617 (1968)

Na, cat (4-*t*-BuC₆H₄)₂, THF, ultrasound

TL 30 4935 (1989)



SL 89 (1990)

*n*

2

JACS 72 983 (1950)

JOC 31 2017 (1966)

TL 1529 (1969)

3

JACS 72 3376 (1950), 75 3997, 6231 (1953)

4

JACS 72 3376 (1950); 79 6050 (1957)

7, 8, 10, 12, 14, 18

Helv 30 1741 (1947)

7-12

JACS 88 4267 (1966)

7-16

Helv 30 1822 (1947)

8

JACS 74 3626 (1952)

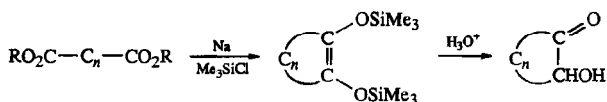
Org Syn Coll Vol 4 840 (1963)

8, 14, 16

Helv 30 1815 (1947)

14

JOC 57 252 (1992)



Review: Syn 236 (1971)

n

2

Ber 100 3820 (1967)

TL 587, 3319 (1968); 28 4669 (1987)

Org Syn 57 1 (1977)

Org Syn Coll Vol 6 167 (1988)

SL 89 (1990) (ultrasound)

JACS 114 6915 (1992)

3

Ber 97 1383 (1964)

JOC 35 1272 (1970)

JACS 111 3319 (1989)

SL 89 (1990) (ultrasound)

4

Ber 97 1383 (1964)

TL 591 (1968)

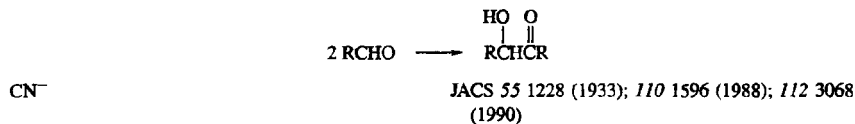
JACS 107 686 (1985)

SL 89 (1990) (ultrasound)

5	Ber 100 3820 (1967) TL 591 (1968) JOC 52 3603 (1987) JACS 110 5479 (1988)
8	Ber 97 1383 (1964) JACS 106 6006 (1984)
10	JACS 106 6006 (1984)
22	JACS 109 7477 (1987)

3. Benzoin and Related Reactions

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 1, Part 2.4, p 541



Org Syn Coll Vol 1 94 (1941)

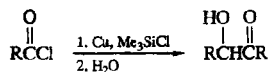
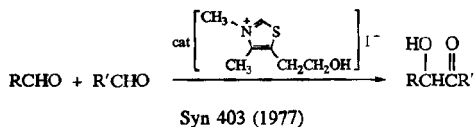
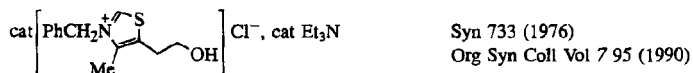
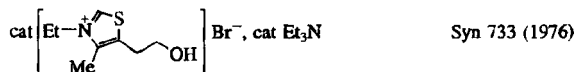
Org Rxs 4 269 (1948) (review)

JOC 57 4033, 4074 (1992); 58 1827 (1993)

Tetr Asym 6 3 (1995)

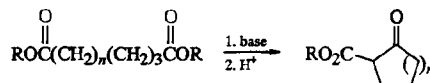
LiTMP

JACS 110 957 (1988)



JOC 53 2381 (1988)

4. Dieckmann and Related Reactions



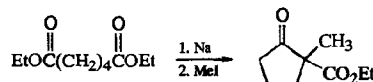
Org Syn Coll Vol 2 116 (1943)

Org Rxs 15 1 (1967) (review)

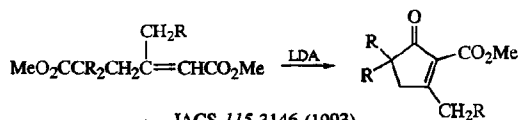
JOC 38 390 (1973); 59 394, 5336 (1994); 60 6198 (1995)

SL 4' 6 (1990); 928 (1995)

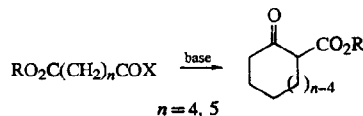
JAC 818 (1992)



Tetr 28 1653 (1972)



JACS 115 3146 (1993)

X

OPh

TL 31 6317 (1990)

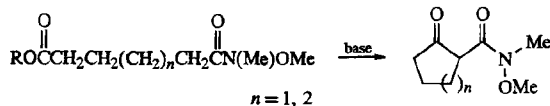
SR

TL 22 1353, 3883 (1981); 24 4837 (1983)

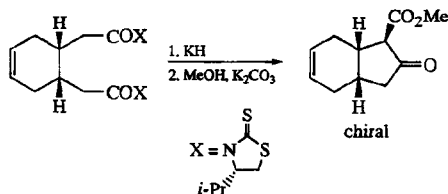
CL 1861 (1987)



JOC 58 2369 (1993)



TL 36 6209 (1995)



JOC 53 5983 (1988)

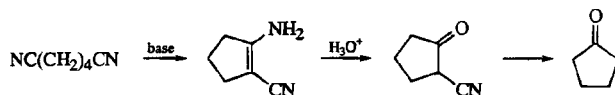
5. Mannich

See page 863, Section 4.

6. Michael

See page 1571, Section 2.

7. Thorpe–Ziegler



JACS 81 4074 (1959); 106 6006 (1984)

Org Rxs 15 1 (1967) (review)

JOC 38 390 (1973)

Org Syn Coll Vol 6 932 (1988)

8. Aldol and Related Reactions

For aldol condensation followed by dehydration, see page 317, Section 3.

General reviews and references:

Org Rxs 16 1 (1968) (aldol); 28 203 (1982) (directed aldol)

BCSJ 53 1417 (1980) (inter- and intramolecular aldol promoted by R_2AlOPh , pyridine)

Can J Chem 59 3303 (1981) (thermal crossed aldol)

TL 22 429 (1981) (intramolecular regioselectivity); 23 4891 (1982) (transition state stereoselectivity); 29 337 (1988) (chiral amide base)

Tetr 38 2279 (retroaldol-aldol), 2939 (intramolecular) (1982)

JACS 104 872 (1982) (intramolecular); 111 8032 (1989) (transition state geometry)

JOC 47 1349 (1982) (intramolecular); 60 6970 (1995) (antibody catalysis)

Topics Stereochem 13 1 (1982) (stereoselectivity)

BCSJ 55 3931 (1982) (retroaldol-aldol)

Syn 294 (1983) [$\text{Si}(\text{OMe})_4$, KF as base]

C. H. Heathcock in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Chpt 2

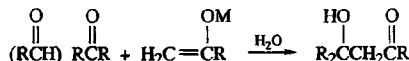
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Parts 1.4–1.7 and 1.9

M. Braun in "Advances in Carbanion Chemistry," Ed. V. Snieckus, JAI Press, Greenwich, Connecticut (1992), Vol 1 (stereoselectivity)

Contemporary Organic Synthesis 1 317 (1994) (asymmetric)

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21b, G. Thieme, Stuttgart–New York (1995), pp 1603–1748

8.1. Metal Enolates

M

Li

JOC 9 (1974); 45 1066, 3846 (1980); 46 191, 1296, 2290 (1981); 48 4. 33; 50 2095 (1985); 52 4062, 4681 (1987); 53 1560, 1922 (1988); 54 3486, 3754 (1989); 55 1114, 2800 (1990); 56 378, 2098, 2499, 2826, 7084 (1991); 57 3599 (enantioselective, chiral base), 5403, 5590 (1992); 58 533 (enantioselective, chiral base), 4191, 4619 (1993); 60 6397 (1995)
 Angew Int 19 557 (1980)
 JACS 103 3099 (1981); 104 5526, 5528 (1982); 105 1667 (1983); 107 5396 (1985); 108 4603 (1986); 109 3353 (1987); 110 4652, 6914 (1988); 111 278, 6648, 7634, 8421 (1989); 112 801, 1597, 3018, 5360, 6965 (1990); 115 1302 (1993); 116 4674 (1994); 117 3448, 6619 (1995)
 TL 24 5233 (1983); 27 3511 (1986); 28 985, 3835, 3839 (1987); 29 2223, 3923, 4119 (1988); 30 5627, 5681 (1989); 31 6001, 6129 (1990); 32 5369 (1991); 33 2501, 3587 (1992); 34 2221, 2711, 8387 (1993); 35 1313, 4485, 4809, 6029, 8537 (1994); 36 961, 3443, 3447 (1995)
 JCS Perkin I 1809 (1983)
 Helv 68 264 (1985)
 CC 1620 (1987) (enantioselective, chiral amide base)
 Org Syn Coll Vol 7 185 (1990)
 SL 361 (1991); 1045 (1994)

Na

TL 35 1313, 4485, 6029 (1994)

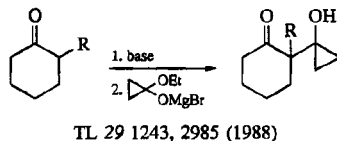
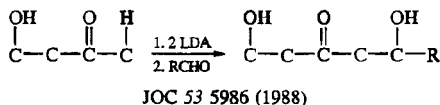
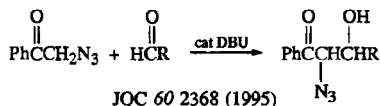
Mg

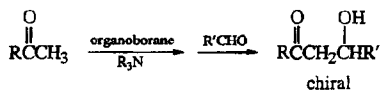
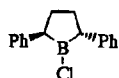
TL 30 6837 (1989)
 JOC 56 2499, 5978, 7084 (1991)

B

CL 153 (1977); 153, 1193 (1981)
 JACS 101 6120 (1979); 103 1566, 1568, 3099 (1981); 104 5521, 5523, 5528 (1982); 107 5292 (1985); 111 3441, 5493 (chiral) (1989); 112 7407 (1990) (chiral); 113 1047 (1991); 114 2995 (1992); 115 1608 (1993); 116 2615, 3623, 11287 (chiral) (1994); 117 6619, 9073 (1995)
 TL 1665, 2225, 2229, 3937 (1979); 21 4291, 4675 (1980); 22 3555 (1981); 23 2387 (1982); 28 1229 (1987); 30 6383, 7121, 7357 (1989); 31 2213, 6129, 7513 (1990); 32 777, 1507, 5239, 5369, 7601 (1991); 33 801, 3587, 7223 (1992); 34 1115, 4389, 4393, 6871 (1993); 35 441, 8537, 9083, 9477 (1994); 36 175, 3443, 3447, 5353 (1995)
 BCSJ 53 174 (1980)
 JCS Perkin I 1809 (1983)
 Pure Appl Chem 55 1749 (1983)
 CC 147 (1983); 1102 (1987)
 JOC 52 1347 (1987); 54 2817 (1989); 55 1709 (1990) (intramolecular); 56 2098, 2499, 5820 (1991); 57 499, 2716, 3261, 3767, 5173, 5590 (1992); 58 147, 4182, 6545, 7162 (1993); 60 3288 (1995)
 Tetr 48 2127 (1992)
 SL 498 (1995)

- Al** CL 379 (1979)
 TL 2257 (1979); 23 2387 (1982)
 Helv 68 264 (1985)
 JOC 57 5590 (1992)
- Sn** CC 162 (1981)
 CL 467 (1982)
 JCS Perkin I 1809 (1983)
 Pure Appl Chem 55 1749 (1983)
 TL 24 3347 (1983); 32 5369 (1991); 33 4233 (1992); 34 4389, 4393
 (1993); 35 6925 (1994); 36 175 (1995)
 JOC 57 5590 (1992)
 JACS 115 1608 (1993); 116 3623, 11287 (1994)
 Org Rxs 46 1 (1994) (review)
- Ti** TL 22 4691 (1981); 31 6001 (1990); 32 5369 (1991); 33 801 (1992); 34
 2229, 2711, 4393, 8387 (1993); 35 4809, 6925, 8537 (1994); 36 175,
 3443, 3447 (1995)
 Topics Curr Chem 106 55 (1982) (review)
 JACS 111 5722 (chiral), 8231 (1989); 113 1047 (1991); 115 9345
 (intramolecular), 11446 (1993); 117 9073 (1995)
 JOC 56 2098, 2499 (1991)
 SL 535 (1993)
- Zr** TL 21 3975, 4607 (1980); 32 5369 (1991)
 JACS 104 5528 (1982)
 JCS Perkin I 1809 (1983)
 JOC 55 5306 (1990); 56 2098 (1991); 57 5590 (1992)
- Zn** JOC 52 3489 (1987)
 Org Syn Coll Vol 6 692 (1988)
 TL 30 5799 (1989); 36 1545 (enantioselective), 5353 (1995)
 JACS 113 7613 (1991)
- Ce** TL 24 5233 (1983); 28 3817 (1987)
- (Et₂N)₃S⁺** JACS 103 2106 (1981)



Organoborane(Ipc)₂BOTf

TL 27 4721 (1986)

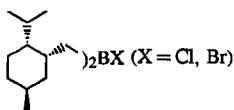
TL 27 4787 (1986); 28 1229 (1987); 29 585 (1988);
30 997, 1293 (1989); 31 2213 (1990); 32 1749
(1991); 33 1767, 3587 (1992); 35 441 (1994)

Chem Ind 390 (1988) (review)

Tetr 46 4663 (1990)

Pure Appl Chem 64 1821 (1992)

JOC 60 3288 (1995)

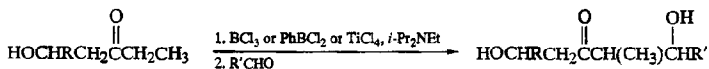
(Ipc)₂BCl

TL 31 2213 (1990); 34 5351 (1993); 35 441 (1994);
36 6383 (1995)

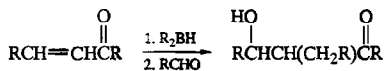
Pure Appl Chem 64 1821 (1992)

Angew Int 32 1618 (1993)

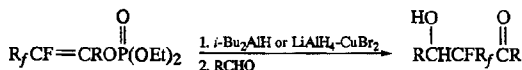
TL 35 4623 (1994)



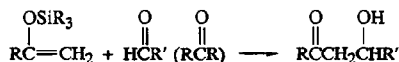
JOC 60 3013 (1995)



TL 32 1229 (1991)



JOC 55 3107 (1990)



JACS 114 7922 (1992)

high pressure

JACS 105 6963 (1983)

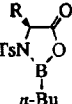

JOC 56 2098 (1991)

H₂O

JOC 51 2142 (1986)

cat (Ph₃C)ClO₄

CL 447, 1535 (1985)

cat (Ph ₃ C)OTf	CL 1535 (1985) JACS 117 4570 (1995)
cat (Ph ₃ C)SbCl ₆	CL 1535 (1985)
cat (Ph ₃ C)PF ₆	CL 1535 (1985)
cat (Ph ₃ C)SnCl ₅	CL 1535 (1985)
BF ₃ ·OEt ₂	JACS 105 1667 (1983); 114 9434 (1992); 117 6619, 9598 (1995) TL 25 5973 (1984); 30 5623, 7435 (1989); 31 5053, 6129 (1990); 35 3405, 8537 (1994) JOC 54 5426 (1989); 56 2098 (1991); 57 5403 (1992) SL 448 (1990)
cat (C ₆ F ₅) ₃ B	SL 577 (1993)
cat BH ₃ -2,6-(<i>i</i> -PrO) ₂ C ₆ H ₃ CO ₂ CH(CO ₂ H)CH ₂ -CHOHCO ₂ H (enantioselective)	JACS 113 1041 (1991)
cat  (enantioselective)	TL 33 6907 (1992)
 (enantioselective)	TL 36 2821 (1995)
AlCl ₃	JOC 53 1560 (1988); 57 5403 (1992) TL 31 5053 (1990)
EtAlCl ₂	TL 30 5623 (1989) JOC 54 83 (1989)
(2,6-Ph ₂ C ₆ H ₃ O) ₃ Al	SL 439 (1994)
cat Me ₃ SiCl, cat SnCl ₂	CL 463 (1987)
cat Me ₃ SiOTf	Chem Pharm Bull 38 1509 (1990) JACS 117 4570 (1995)
cat SnCl ₂ , cat Ph ₃ CCl	CL 491 (1987)
cat <i>n</i> -Bu ₂ Sn(OTf) ₂	JACS 112 901 (1990)
<i>n</i> -Bu ₃ SnF, cat PdCl ₂ (PAr ₃) ₂	TL 24 5001 (1983)
SnCl ₄	TL 24 3347 (1983); 25 5973 (1984); 31 5053 (1990) JOC 56 2098 (1991); 57 5403 (1992) SL 275 (1994)
cat <i>n</i> -Bu ₄ NF	JACS 99 1265 (1977) JOC 48 932 (1983); 56 2098 (1991) TL 29 2207 (1988); 31 2067 (1990)

cat R_4NF (enantioselective)	TL 34 1507 (1993)
cat $(Ph_4P)HF_2$	SL 1033 (1995)
cat $BiCl_3$	TL 29 4719 (1988) BCSJ 64 990 (1991) JOC 58 1835 (1993)
cat $BiCl_3$, cat NaI	TL 33 1053 (1992) JOC 58 1835 (1993)
cat $BiCl_3$, cat SnI_2 or ZnI_2	JOC 58 1835 (1993)
$[(Et_2N)_3S]Me_3SiF_2$	JACS 103 2106 (1981)
cat $Sc(OTf)_3$	SL 472 (1993)
$TiCl_4$	CL 1223 (1974) JACS 96 7503 (1974); 107 5292 (1985) Angew Int 16 817 (1977); 22 989 (1983) TL 24 3341, 3343 (1983); 25 5973 (1984); 27 3369 (1986); 28 985 (1987); 29 3885 (1988); 31 5053 (1990); 33 1903, 4675 (1992); 35 4809 (1994) JOC 50 2375 (1985); 52 120 (1987); 53 4864 (1988); 54 83, 840 (1989); 55 1114, 3982 (1990); 56 1133, 1325, 2098, 7084 (1991); 57 5403 (1992); 60 6499 (1995) Org Syn 65 6 (1987) Org Syn Coll Vol 8 323 (1993)
cat $Ti(O-i-Pr)_4$, BINOL (enantioselective)	JOC 60 5998 (1995)
cat $Cp_2Ti(OTf)_2$	TL 33 6423 (1992) JACS 117 4570 (1995)
cat $Cp_2Zr(OTf)_2$	TL 33 6423 (1992)
cat $Zr(OTf)_2(tmtaa)$ (tmtaa = dibenzotetramethyltetraazaannulene)	SL 857 (1994)
cat $[HC(py)_3W(NO)_2(CO)](SbF_6)_2$	TL 34 2275 (1993)
cat $[Ru(salen)(NO)H_2O]SbF_6$	TL 33 5729 (1992)
cat $[(COD)Rh(dppb)]X$ ($X = PF_6, ClO_4$) or $Rh_4(CO)_{12}$	TL 27 5517 (1986)
cat $[Rh(NBD)(dppe)]ClO_4$	TL 28 793 (1987)
cat $H_2C=C(Ph)ORh(CO)(PMe_3)_2$	JACS 111 938 (1989)
cat $PdCl_2(BINAP)$, $AgOTf$, H_2O (enantioselective)	JOC 60 2648 (1995)
$ZnBr_2$	TL 31 5053 (1990) JOC 57 5403 (1992)
cat SmI_2	TL 34 3881 (1993)

cat $\text{Ln}(\text{OTf})_3$ ($\text{Ln} = \text{Gd}, \text{Yb}, \text{Lu}$), H_2O

CL 2187 (1991)

TL 33 1625 (1992); 36 1633 (1995)

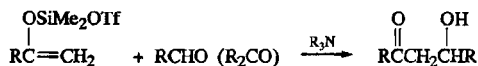
cat $\text{Yb}(\text{OTf})_3$

Syn 371 (1993)

JOC 59 3590 (1994)

various reagents

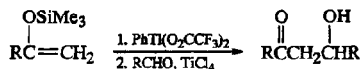
JOC 59 707 (1994)



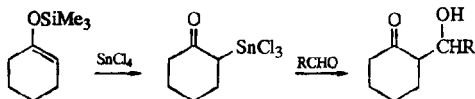
JOC 58 2647 (1993)



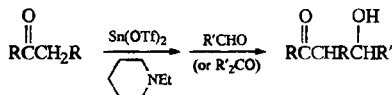
TL 33 1351 (1992)



JOC 53 1022 (1988)

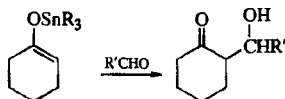


TL 24 3347 (1983)

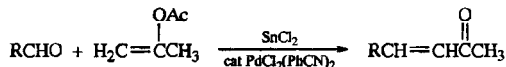


CL 353, 1441 (enantioselective with chiral diamine), 1459, 1601 (1982); 595 (1983)

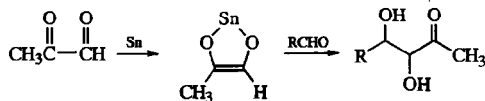
Org Rxs 46 1 (1994) (review)

TL 23 627 (1982); 35 8627 (1994) (with and without cat Ph_4SbBr)

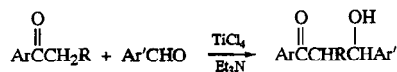
CL 851 (1983)



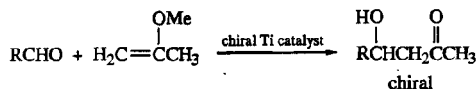
TL 34 653 (1993)



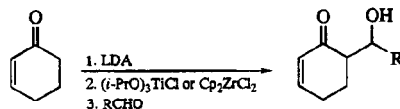
CL 1825 (1983)



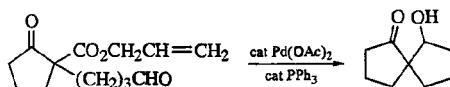
TL 28 4135 (1987)



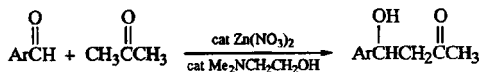
JACS 117 3649 (1995)



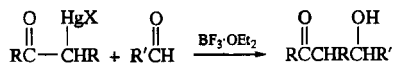
TL 29 1661 (1988)



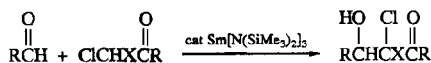
JACS 111 4126 (1989)



TL 36 4009 (1995)

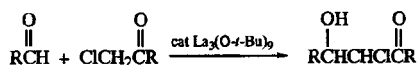


JACS 104 2323 (1982)

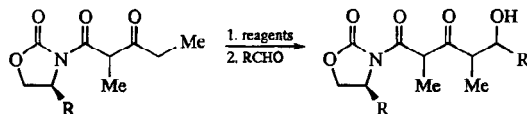
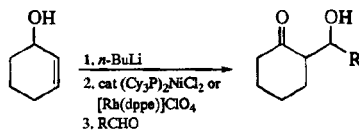


X = H, Cl

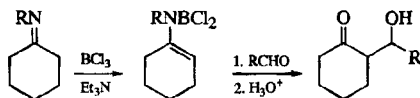
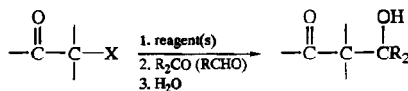
JOC 59 2661 (1994)



JACS 114 4418 (1992)

ReagentsCy₂BCl, EtNMe₂Tetr 48 2127 (1992)
JACS 115 11446 (1993)Sn(OTf)₂, Et₃NJOC 55 5192 (1990)
JACS 112 866 (1990); 117 3448 (1995)TiCl₄, *i*-Pr₂NEtJACS 112 866 (1990); 114 9434 (1992)
JOC 57 1958 (1992)**8.2. Related Reactions**

TL 33 6187 (1992)

TL 1423 (1979) (enantioselective)
Syn Commun 9 515 (1979)

X = halogen

Reagent(s)Et₃B, Ph₃SnH

TL 29 1041 (1988)

Sn

CL 467 (1982), 1727 (1983)

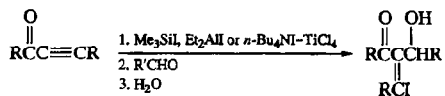
CuCl, Zn

TL 28 6481 (1987)

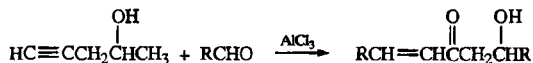
CuBr, Zn, Et₂AlClJACS 99 7705 (1977)
BCSJ 53 3301 (1980)
JOC 53 1227 (1988)
TL 33 4041 (1992)

Zn

JACS 89 5727 (1967)
TL 29 2291 (intramolecular), 2943 (1988)



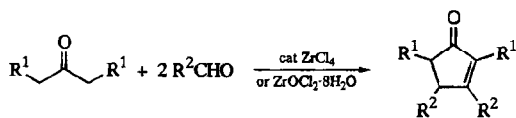
TL 27 4767 (1986)



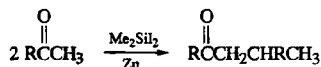
TL 30 4065 (1989)

9. Other Condensation Reactions

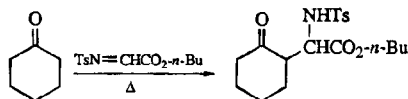
See also page 1475, Section 1.



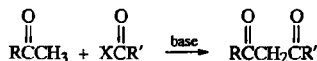
JOC 58 4497 (1993)



CL 1255 (1980)

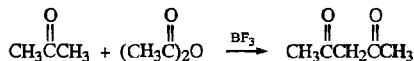


TL 22 4323 (1981)

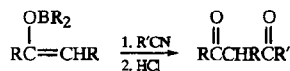


X = Cl, OR

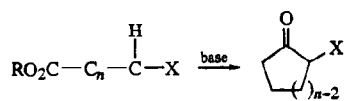
See page 1389, Section 2.6 for acid halides and page 1403, Section 2.8 for esters.



See page 1400, Section 2.7.



See page 1420, Section 2.17.



$\text{X} = \text{CN}, \text{SOPh}, \text{SO}_2\text{Ph}$

See page 1403, Section 2.8.

6. CYCLIZATION AND ANNULATION REACTIONS

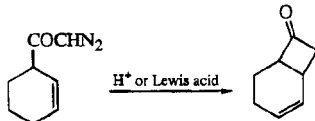
Reviews:

Tetr 32 3 (1976)

Syn 177 (1976)

1. Cyclization

See also page 1422, Section 3.



CC 876 (1974); 746 (1981)

Org Rxn 26 361 (1979) (review)

JCS Perkin I 1924 (1980); 1203 (1981)

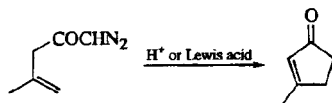
TL 21 691 (1980)



Org Rxn 26 361 (1979) (review)

Tetr 37 2407 (1981) (review)

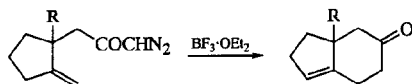
J Chem Res (S) 5 (1981)



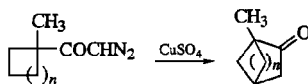
Org Rxn 26 361 (1979) (review)

JACS 103 1996, 2009, 2017 (1981)

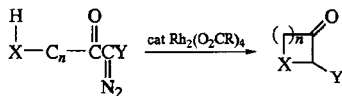
Tetr 37 2407 (1981) (review)



JACS 113 5765 (1991)

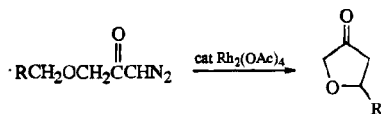
 $n = 1 - 4$

JOC 47 3242 (1982)

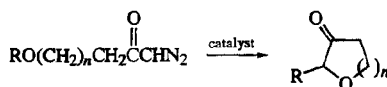


<u>Y</u>	<u>X</u>	<u>n</u>	
H	C	1	JACS 115 8669 (1993) (β -lactam)
		2	JACS 107 5732 (1985); 109 5432 (1987); 114 1874 (1992) (cyclopentanone, 2-indanone); 115 8669 (1993) (cyclopentanone, 2-indanone, pyrrolidone); 116 3296 (1994)
			TL 28 165 (2-indanones); 4773 (1987); 29 2283 (1988); 36 1491 (1995) (chiral, 2-indanones)
			JOC 56 1434 (1991)
		3	CC 129 (1984) (2-tetralones)
			TL 26 6035 (1985)
			JOC 54 299 (1989)
R	C	2	JOC 57 436 (1992)
COR	C	1	JACS 115 8669 (1993) (β -lactam)
		2	JACS 115 8669 (1993) (pyrrolidone)
CO ₂ R	C	1	JACS 106 5295 (1984)
			TL 28 637 (1987)
		2	JOC 47 4808 (1982); 52 28 (1987)
			JACS 105 5935 (1983); 106 5295 (1984); 107 196, 5289 (1985); 108 7686 (1986)
			TL 26 3059 (1985); 28 637, 5351 (1987); 31 3995, 5173 (chiral) (1990); 33 2709 (1992); 34 5109 (1993) (chiral); 35 7269 (1994) (chiral)
			SL 353 (1994) (chiral R, enantioselective)
		3	TL 24 5453 (1983) (2-hydroxynaphthalene-1-carboxylate ester)
	N	1-3	TL 21 31, 2783 (1980); 23 3105 (1982); 28 781 (1987)
			JOC 50 5223 (1985)
			JACS 108 6054 (1986)

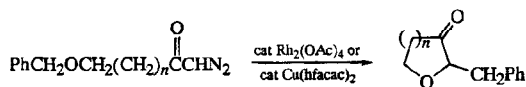
	O	4, 5	TL 27 1403 (1986)
		5	TL 28 5351 (1987)
	O or S	2	JOC 50 5223 (1985)
SO ₂ Ph	C	3, 4	TL 28 5351 (1987)
		2	TL 28 3459 (1987)
			JOC 52 5742 (1987)
PO(OEt) ₂	C	2	SL 990 (1992)
			SL 575 (1991)



TL 30 1749, 1753 (1989); 33 1143 (1992)

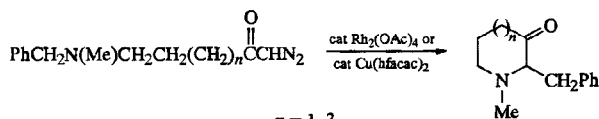
**Catalyst**

	<i>n</i>	
Rh ₂ (OAc) ₄	1, 2	TL 33 5983 (1992); 34 4385 (1993) JOC 57 3479 (1992)
Cu(acac) ₂	1, 2	TL 33 6193 (1992); 34 4385 (1993)
Cu(CF ₃ COCHCOCH ₃) ₂	2	TL 34 4385 (1993)
Cu(CF ₃ COCHCOCF ₃) ₂	2-4	TL 34 4385 (1993); 35 6381 (1994)



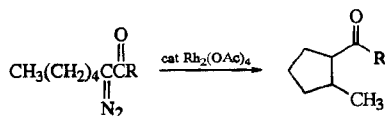
n = 1, 2

JOC 59 6892 (1994)

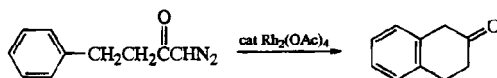


n = 1-3

JOC 59 6892 (1994)



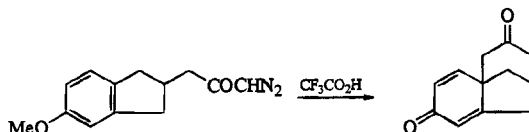
JOC 57 436 (1992)



CC 129 (1984)

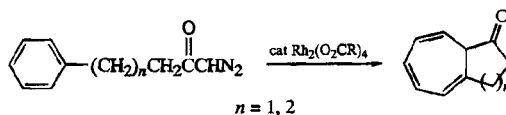


CC 1150 (1987)



Ind J Chem B 2/ 269 (1982)

TL 36 2315, 2527 (1995)

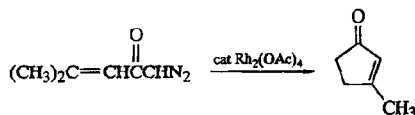


CC 129 (1984)

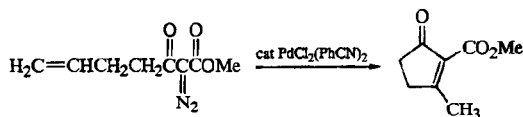
TL 31 4657 (1990); 33 5983 (1992); 36 3397 (1995)

JACS 115 8669 (1993)

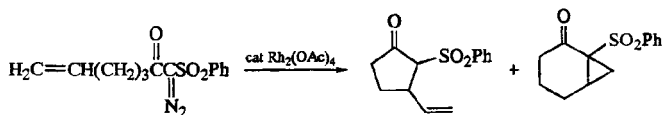
Org Syn Coll Vol 8 196 (1993)



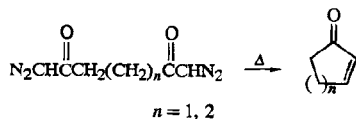
JOC 55 311 (1990); 56 7065 (1991)



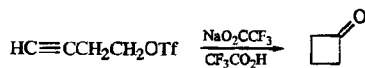
JOC 51 3382 (1986)



TL 28 3459 (1987)

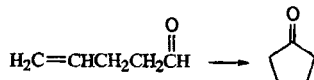


JOC 60 2466 (1995)



Ann 746 211 (1971)

Org Syn Coll Vol 6 324 (1988)

SnCl₄

TL 1287 (1972)

CC 146 (1979)

"ClRh(PAr₃)₂"

TL 1287 (1972); 30 6349 (1989); 32 3473 (1991)

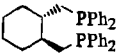
JACS 98 1281 (1976); 100 640 (1978); 101 489

(1979); 102 190 (1980); 116 1821 (1994) (chiral)

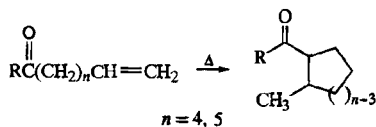
Chem Pharm Bull 34 550 (1986)

Rh(BINAP)ClO₄ (enantioselective)

TL 33 6331 (1992); 34 5927 (1993)

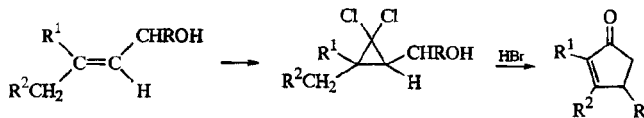
[RhCl(cyclooctene)]₂,  (enantioselective)

Tetr 47 4879 (1991)



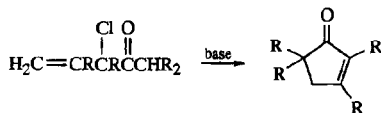
Syn 1 (1975) (review)

Tetr 36 1195 (1980)

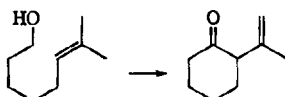
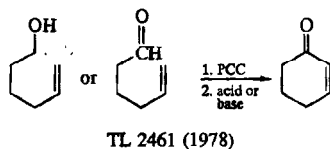
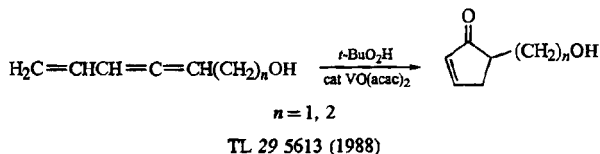
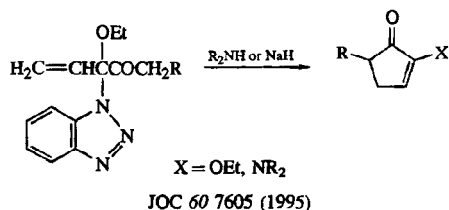


JACS 96 3713 (1974)

BCSJ 53 1010 (1980)



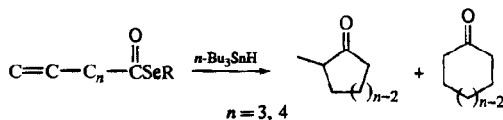
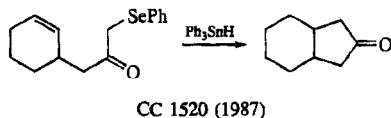
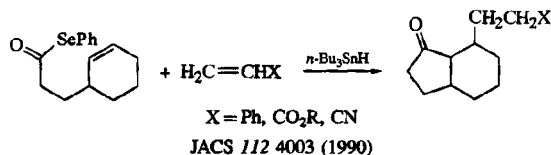
JOC 56 713 (1991)

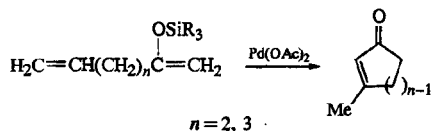
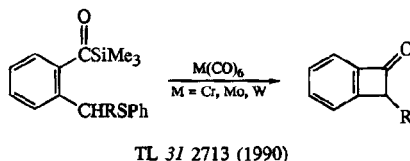
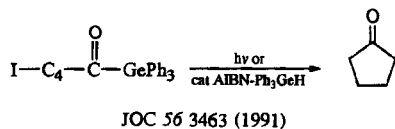
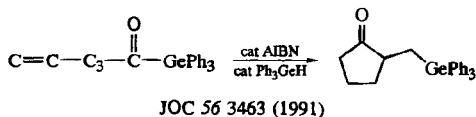


PCC

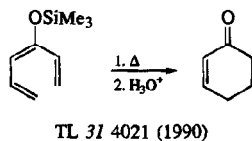
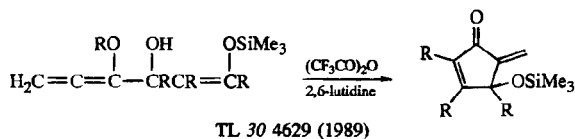
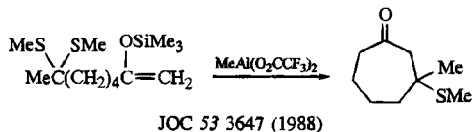
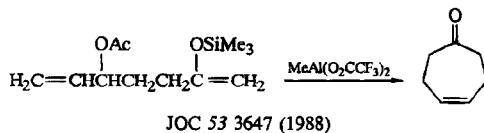
JOC 41 380 (1976); 50 2668 (1985)
TL 2461 (1978) CrO_3 , py, $\text{CF}_3\text{CO}_2\text{H}$

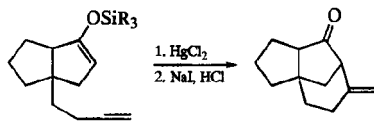
Can J Chem 55 1039 (1977)

TL 28 2895 (1987); 29 2585 (1988); 33 875 (1992); 35 2593 (1994)
JOC 53 3377 (1988); 57 1429 (1992)
JACS 112 9272 (1990)



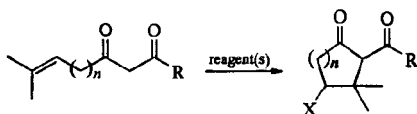
JACS 101 494 (1979); 102 4519 (1980); 104 1784, 5808 (1982); 108 2090 (1986)
 TL 27 2223 (1986); 32 5911 (1991); 34 5947, 6099 (1993)
 SL 597 (1994); 761 (1995)



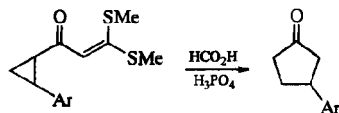


JACS 107 1726 (1985)

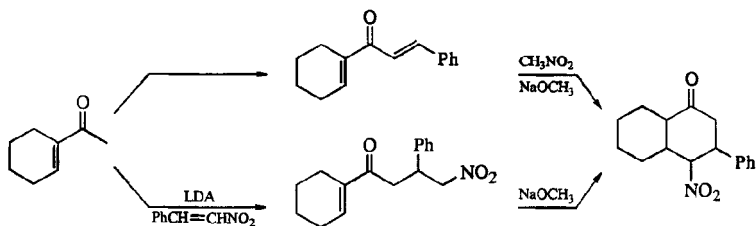
TL 28 3923 (1987); 34 7889 (1993)



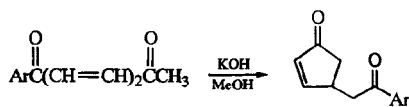
<u>n</u>	<u>R</u>	<u>Reagent(s)</u>	<u>X</u>	
2	Me, OMe	SnCl ₄	H	Angew Int 20 687 (1981)
	OMe	PhSCL, silica gel	PhS	Can J Chem 59 2239 (1981)
		PhSeCl, AlCl ₃	PhSe	Can J Chem 59 2239 (1981)
3	OMe	SnCl ₄	H	Angew Int 20 687 (1981)



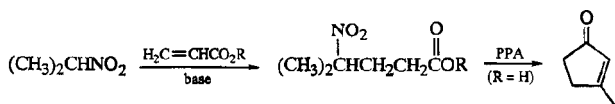
TL 29 2111 (1988)



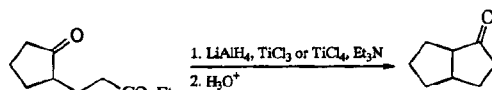
TL 28 2945 (1987)



JOC 59 7915 (1994)



CC 1149 (1980)



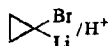
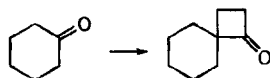
JACS 105 1660 (1983)

TL 24 1885 (1983)

CC 1607 (1987)

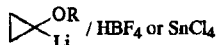
2. Spiroannulation

Review: Syn 383 (1974) (Synthesis of Carbocyclic Spiro Compounds via Intramolecular Alkylation Routes)



TL 3295 (1974)

Ber 108 2368 (1975)

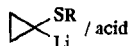


TL 22 2455 (1981)

Helv 64 2598 (1981)

JOC 50 3255 (1985)

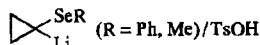
Org Syn Coll Vol 8 556 (1993)



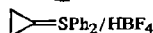
Ber 108 2368 (1975)

JACS 99 3080 (1977)

TL 22 2455 (1981); 23 4385 (1982)

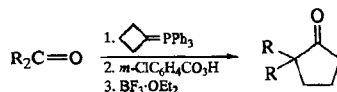


TL 23 4385 (1982)

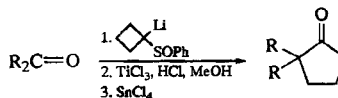


JACS 95 5321 (1973)

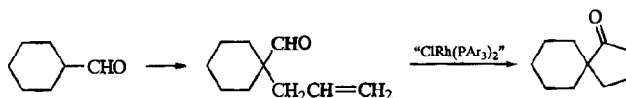
Acct Chem Res 7 85 (1974)



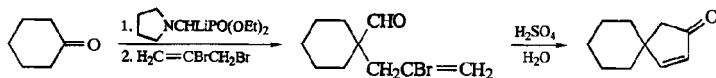
TL 29 5525 (1988)



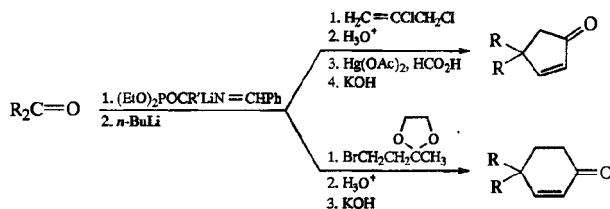
TL 36 4985 (1995)



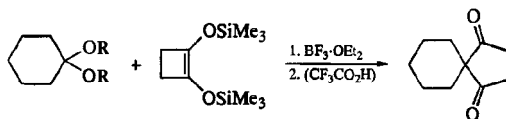
JACS 102 190 (1980)



JOC 42 2520 (1977); 43 1027 (1978)



JACS 102 5866 (1980)



JACS 106 1759 (1984)

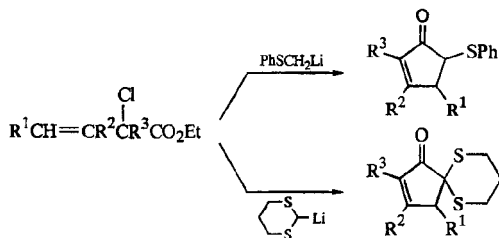
TL 29 4369 (1988)

Org Syn Coll Vol 8 578 (1993)

JOC 59 104, 1485 (1994)

3. One-Carbon Annulation

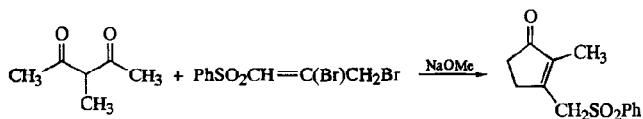
See also page 1363, Section 7.



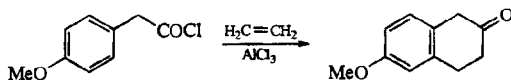
JOC 55 5294 (1990)

4. Two-Carbon Annulation

See also page 1308, Section 9.15.

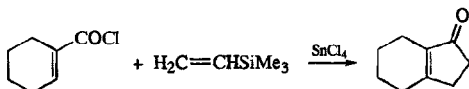


TL 31 6145 (1990)



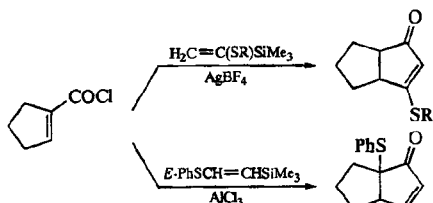
JOC 26 4232 (1961)

Org Syn Coll Vol 6 744 (1988)



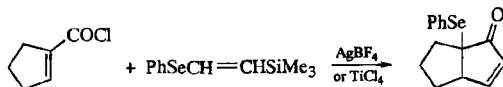
TL 1995, 1999 (1979)

JOC 45 1046, 3017 (1980)

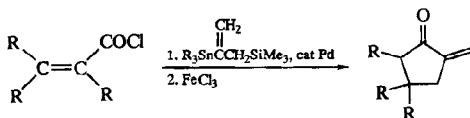


Organomet 1 1240, 1243 (1982)

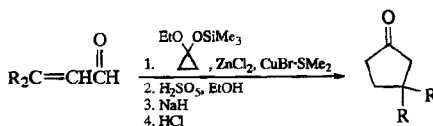
JOC 50 1621 (1985)



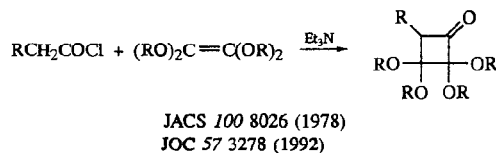
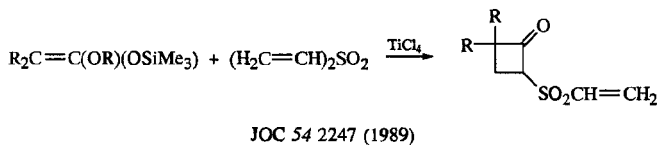
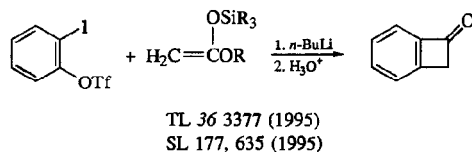
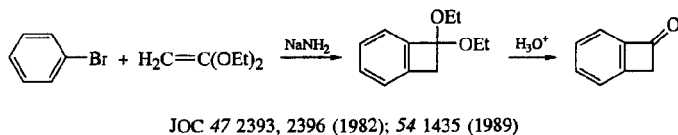
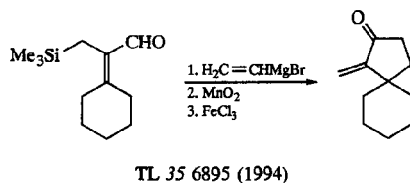
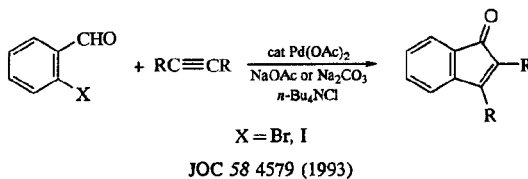
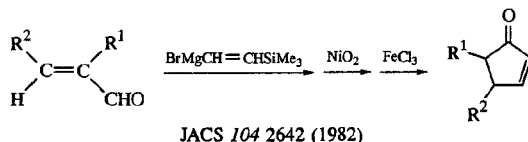
TL 31 2917 (1990)

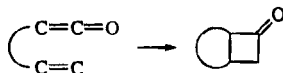


TL 33 3495 (1992)



JOC 59 5496 (1994)





JACS 107 2192 (alkyl and vinyl ketene), 2194 (alkoxy ketene), 4339 (vinyl ketene) (1985); 110 649 (1988) (alkyl ketene)

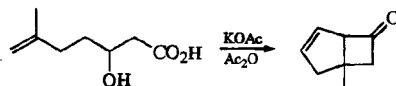
TL 26 3535 (vinyl ketene), 5619 (vinyl ketene) (1985); 27 1913 (imino ketene), 5471 (vinyl ketene) (1986); 29 459 (vinyl ketene), 1493, 2303 (ketene and vinyl ketene), 3175, 3201 (1988); 31 219 (1990); 32 4623 (1991); 35 2949 (1994); 36 2729 (1995)

JOC 50 2809 (vinyl ketenes), 5167 (alkoxy ketene), 5177 (phenoxy ketene) (1985); 52 307 (chloro ketene), 1568 (vinyl ketene), 5413 (vinyl ketene) (1987); 53 1848, 2356, 4508, 5320 (1988) (all vinyl ketenes); 55 3498 (1990); 56 321, 1453, 3358 (all vinyl ketenes), 6094 (1991); 59 5419 (1994)

Ind J Chem B 26 399 (1987)

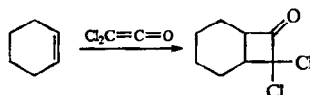
Chem Rev 88 793 (1988) (review)

SL 36 (1989); 729 (1990) (vinyl ketene)



Tetr 50 3235 (1994)

JOC 59 7529 (1994)



Tetr 27 615 (1971); 37 2949 (1981) (review)

Syn 415 (1971) (review)

JOC 43 2879 (1978); 47 3871, 3881 (1982); 48 4763 (1983); 50 3957 (1985); 52 3693, 4885 (1987); 56 6829 (1991); 57 4567 (1992); 58 7537 (1993); 59 1199 (1994); 60 4940 (1995)

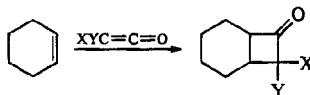
Helv 64 64 (1981)

JACS 105 2435 (1983); 106 5295 (1984); 108 8015 (1986); 109 4752 (1987) (asymmetric); 114 10084 (1992)

TL 29 5661 (1988); 30 565, 7065 (1989); 32 6011 (1991); 34 27, 8157 (1993); 35 3865 (1994)

Org Syn Coll Vol 6 1037 (1988); 8 377 (1993)

SL 511 (1991)



Reviews:

Org Rxs 3 108 (1946) (preparation of ketenes); 12 26 (1962); 45 159 (1994)

J Chem Ed 53 81 (1976)

Chem Soc Rev 10 289 (1981) (cyano ketenes)

Chem Rev 86 821 (1986) (conjugated ketenes)

X

Y

H

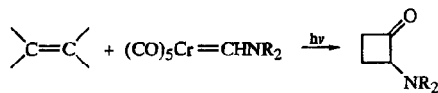
R

TL 36 5109 (1995)

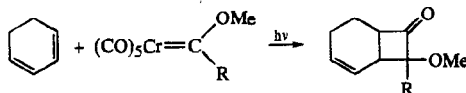
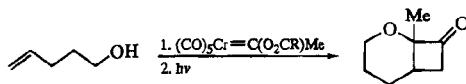
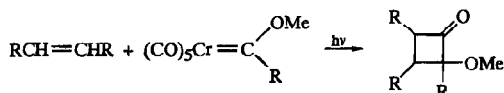
Me

Me₃SiO

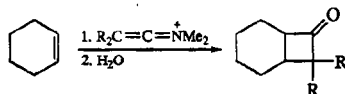
JACS 110 4456 (1988)



JOC 56 2209 (1991)



JACS 112 4364 (1990)



JACS 94 2870 (1972); 104 2920 (1982); 107 2192, 2194 (1985) (both intramolecular)

Angew Int 20 782, 879 (1981)

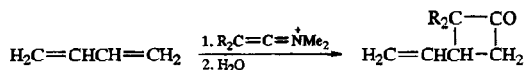
JOC 50 5169 (1985) (intramolecular); 52 2216 (1987) (intramolecular); 57 7163 (1992)

TL 27 5211 (1986) (intramolecular); 29 3369 (1988) (intramolecular); 31 4467 (1990) (intramolecular); 32

3827 (1991); 33 7357 (1992) (chiral); 36 2729 (1995) (intramolecular)

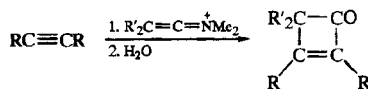
Chem Rev 88 793 (1988) (intramolecular, review)

Org Syn Coll Vol 8 306 (1993)



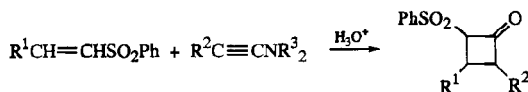
JACS 94 2870 (1972)

Syn 706 (1981)

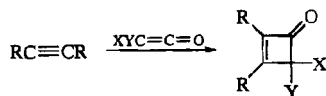


Angew Int 14 569 (1975); 20 879 (1981)

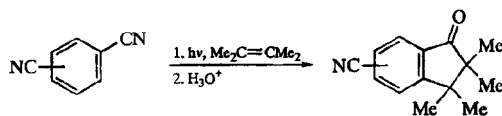
TL 25 5043 (1984)



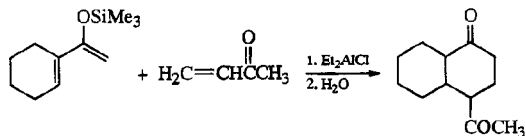
JOC 47 1608 (1982)



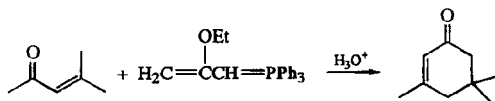
<u>X</u>	<u>Y</u>	
H	H	TL 1031 (1962) JOC 38 1451 (1973) JACS 110 3693 (1988) JOC 58 3942 (1993)
	Cl	
Me	Me	TL 1031 (1962) JOC 38 1451 (1973)
—(CH ₂) ₄ —		JOC 38 1451 (1973)
CF ₃	CF ₃	JOC 35 3308 (1970)
Ph	Ph	TL 1031 (1962) JCS 2708 (1962) Helv 45 600 (1962)
Ar	Ar	Tetr 36 2291 (1980)
Cl	Cl	Ann 722 232 (1969); 2074 (1974) JACS 96 2267 (1974); 114 10980 (1992) TL 2715 (1976); 24 23 (1983) Syn 689 (1979) JOC 48 3382 (1983) Org Syn Coll Vol 8 82 (1993) JOC 50 3226 (1985)
	CN	



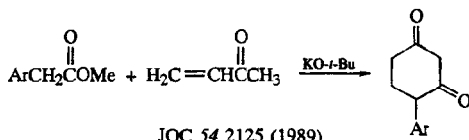
TL 35 8485 (1994)



CC 1333 (1987)

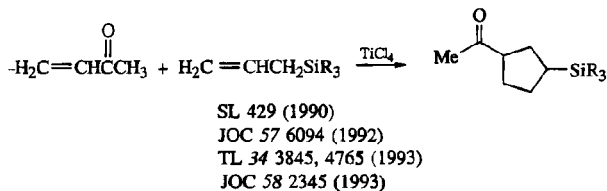
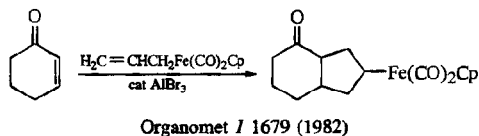
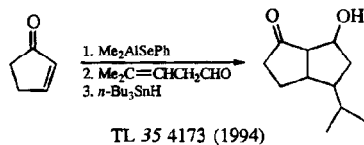
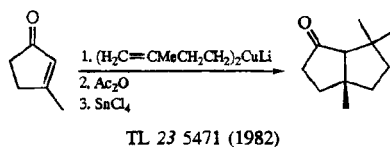
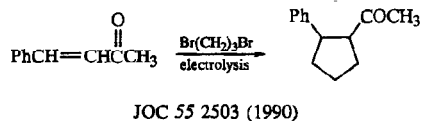
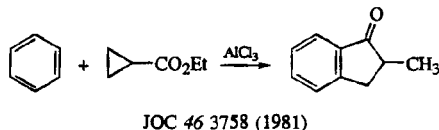


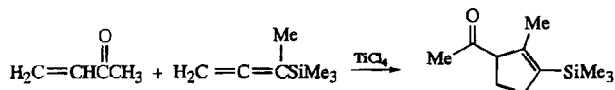
JOC 42 1664 (1977)



5. Three-Carbon Annulation

Review: Syn 529 (1984)



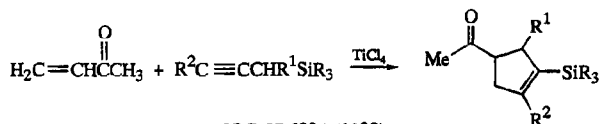


JOC 103 1604 (1981)

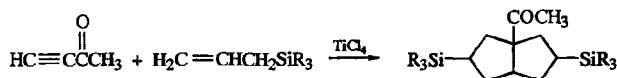
Tetr 39 935 (1983)

Org Syn Coll Vol 8 347 (1993)

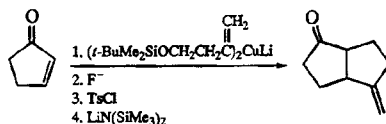
SL 941 (1995)



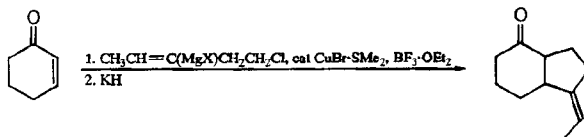
JOC 57 6094 (1992)



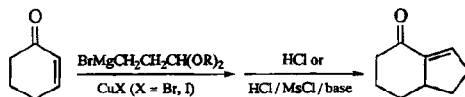
SL 131 (1994)



Organomet 1 1243 (1982)



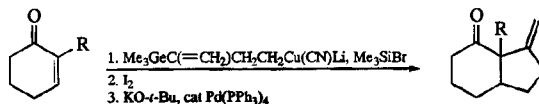
JOC 55 2380 (1990)



TL 4217 (1978)

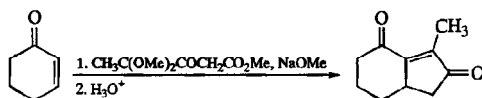
JACS 104 6081 (1982); 105 7352 (1983); 106 1442 (1984)

JOC 47 5045 (1982)

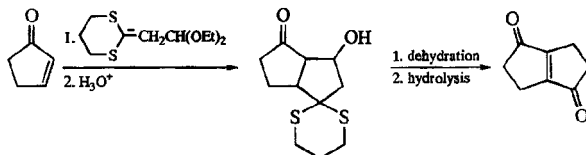


JOC 55 3454 (1990)

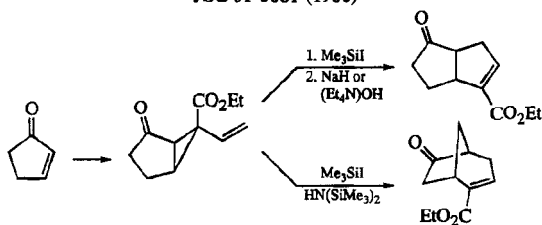
TL 36 5857 (1995)



JOC 47 4791 (1982)

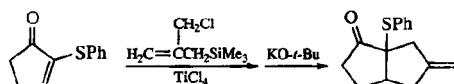


JOC 51 3861 (1986)

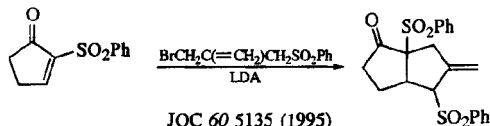


TL 28 167 (1987)

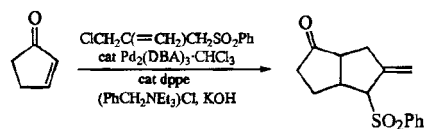
JOC 55 2570 (1990)



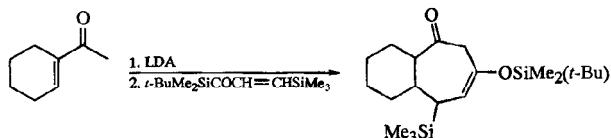
TL 21 4557 (1980)



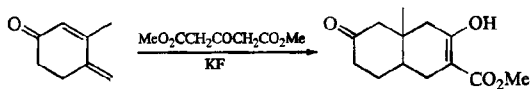
JOC 60 5135 (1995)



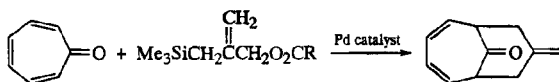
TL 29 201 (1988)



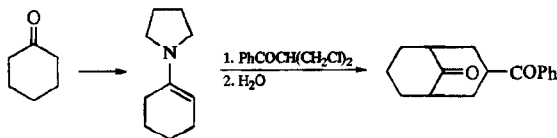
JACS 117 6400 (1995)



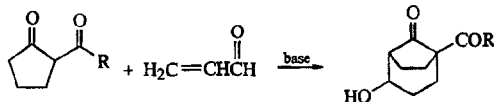
JCS Perkin I 25 (1982)



JACS 109 615 (1987)



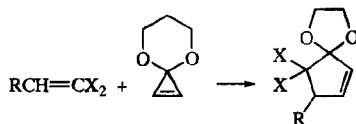
Ann 1322 (1974)



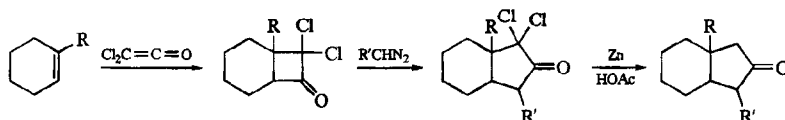
JOC 60 6872 (1995)



Can J Chem 60 2965 (1982)

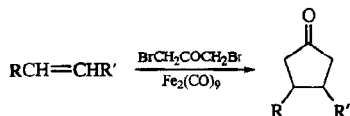


See page 547, Section 3.

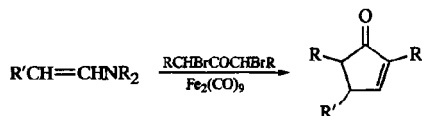


JACS 101 4003 (1979); 105 2435 (1983); 106 5295 (1984); 108 8015 (1986); 109 4752 (1987) (asymmetric)
 JOC 45 2036 (1980); 48 4763 (1983); 50 3957 (1985); 56 7048 (1991)

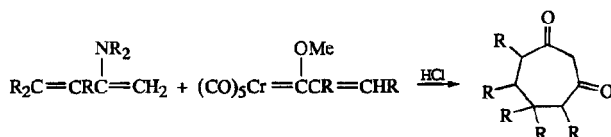
See also page 1338, Section 4.



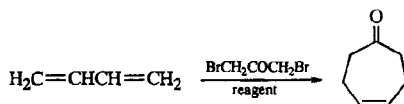
JACS 94 7202 (1972); 95 2722 (1973); 99 5196 (1977); 101 220 (1979) (intramolecular); 105 7358 (1983)
 TL 4347 (1976); 993 (1978)
 Acct Chem Res 12 61 (1979) (review)
 Org Rxn 29 163 (1983) (review)



JACS 94 1772 (1972); 99 5196 (1977); 100 1799 (1978)
 Acct Chem Res 12 61 (1979) (review)
 Org Rxn 29 163 (1983) (review)
 Org Syn Coll Vol 6 520 (1988)
 JOC 55 2878 (1990)



JACS 117 9419 (1995)



Review: Org Rxn 29 163 (1983)

Reagent(s)

$\text{Fe}_2(\text{CO})_9$

JACS 93 1272 (1971); 99 5196 (1977); 100 1765 (1978); 101 220 (1979) (intramolecular)
 TL 1741 (1973); 1049 (1974); 27 2881 (1986); 34 8123 (1993)
 JOC 40 806 (1975)
 Acct Chem Res 12 61 (1979) (review)

Zn , $\text{B}(\text{OEt})_3$

TL 4487 (1975)

Zn-Cu

JACS 94 3940 (1972); 96 5466 (1974)
 Syn 902 (1978)
 TL 36 1397 (1995)

Zn-Cu , ultrasound

TL 27 687 (1986)

Reagent(s)Zn-Cu, Me₃SiCl

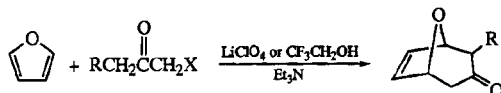
Syn 902 (1978)

Ber 117 3325 (1984)

TL 33 3465 (1992)

Cu, NaI

Org Syn Coll Vol 6 512 (1988)



X = halogen, OMs

TL 21 3005 (1980); 25 1773 (1984); 34 789 (1993) (intramolecular); 36 1397 (1995) (intramolecular)

Angew Int 21 137 (1982)

Syn 976 (1982)

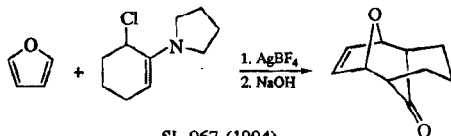
Ber 115 355 (1982); 117 2580 (1984) (intramolecular); 119 524, 1661 (1986); 120 1815, 1951 (1987); 121 1585 (1988)

J Chem Res (S) 128 (1986); 136 (1991); 253 (1993)

Helv 73 1504 (1990) (intramolecular)

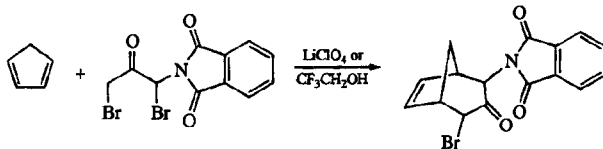
JOC 59 1241 (1994) (intramolecular)

JACS 117 10914 (1995)

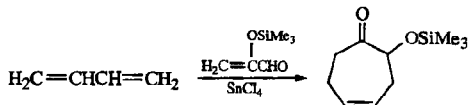


SL 967 (1994)

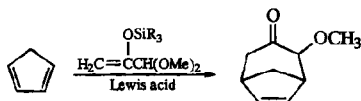
JOC 60 792 (1995)



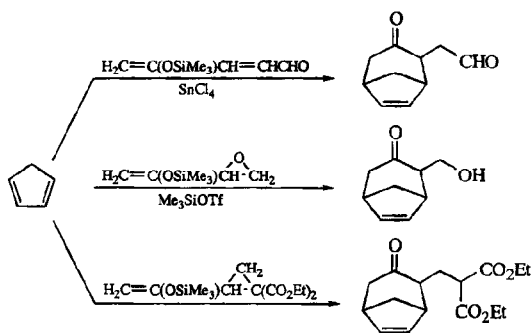
TL 36 23 (1995)



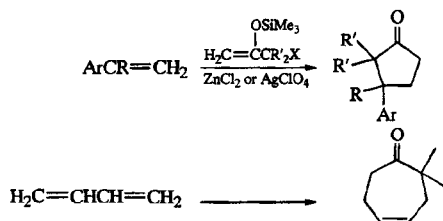
TL 23 1693 (1982)



TL 31 4109 (1990)



JOC 55 6086 (1990)

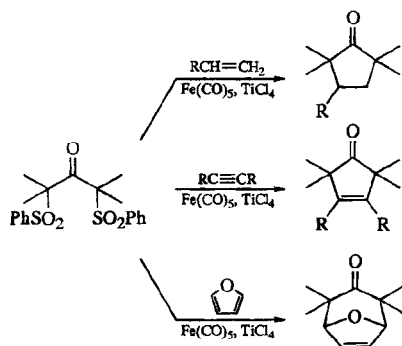


Angew Int 18 163 (1979)

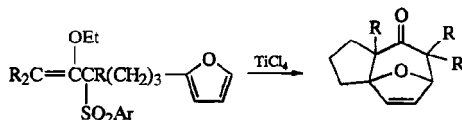
CL 103 (1979)

JACS 104 1330 (1982)

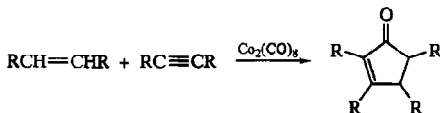
TL 27 2881 (1986)



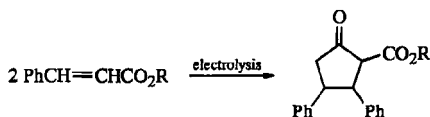
JOC 60 1104 (1995)



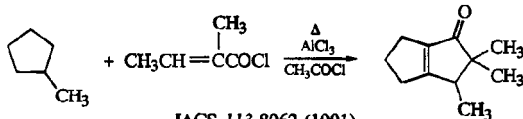
JOC 53 6154 (1988); 59 1241 (1994); 60 5077 (1995)
 TL 31 5981 (1990)



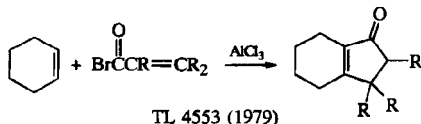
See page 1371, Section 14.



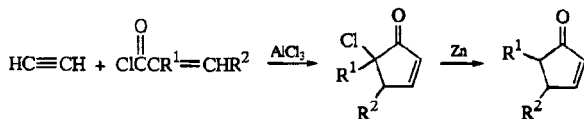
JOC 38 3390 (1973)
 CC 492 (1981)
 TL 35 1897 (1994)



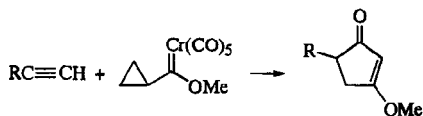
JACS 113 8062 (1991)



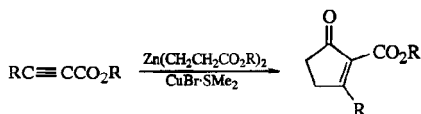
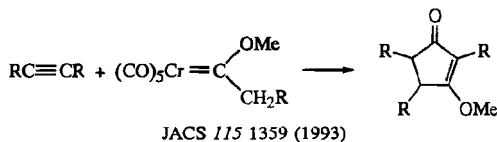
TL 4553 (1979)



Compt Rend C 266 478 (1968)
 BSCF 3098 (1970)
 TL 3131 (1970); 4413 (1976)
 Tetr 28 4027 (1972)
 JOC 45 2224 (1980); 52 5280 (1987)



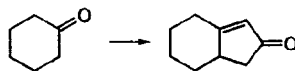
JACS 110 3334 (1988); 114 8394 (1992)



JOC 55 4235 (1990); 58 1038 (1993)

JACS 115 3146 (1993)

TL 35 1657 (1994)

LDA / $\text{BrCH}_2\text{C}(\text{OEt})=\text{CHPO}(\text{OMe})_2$ /
 $\text{H}_3\text{O}^+ / \text{NaH}$

TL 3279 (1979)

Can J Chem 60 1114 (1982)

LDA / $\text{BrCH}_2\text{COCH}=\text{PPh}_3$

Angew Int 18 940 (1979)

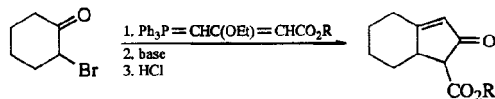
LDA / $\text{ClCH}_2\text{C}(\text{=CH}_2)\text{O}_2\text{P}(\text{OEt})_2$,
cat $\text{Pd}(\text{PPh}_3)_4 / \text{NaOH}$, Δ

TL 27 1115 (1986)

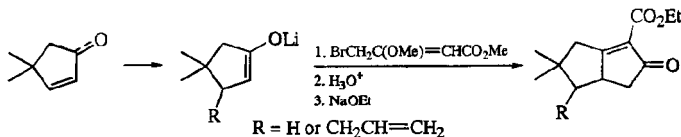
JOC 52 1440 (1987)

 Me_3SiCl , $\text{Et}_3\text{N} / \text{H}_2\text{C}=\text{C}(\text{NO}_2)\text{CH}_3$,
 $\text{SnCl}_4 / \text{H}_2\text{O} / \text{OH}^-$

JACS 98 4679 (1976); 106 2149 (1984)

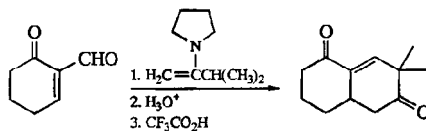


TL 32 4521 (1991)

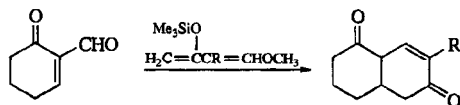


JACS 104 6646 (1982)

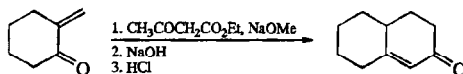
TL 27 5245 (1986)



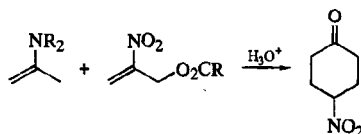
TL 27 1449 (1986)

R = H, CH₃

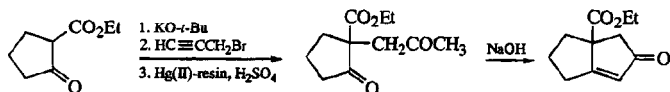
JOC 53 93 (1988)



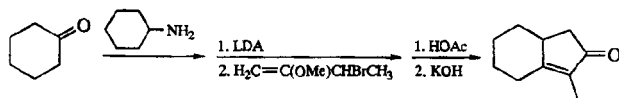
JOC 60 3619 (1995)



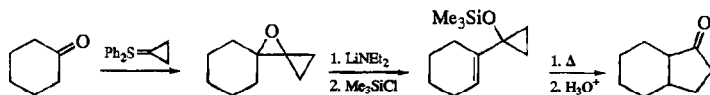
JACS 112 7625 (1990)



JOC 46 2815 (1981)



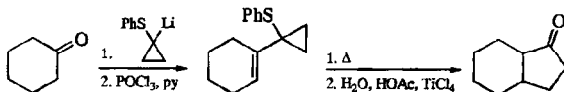
JOC 43 4650 (1978)



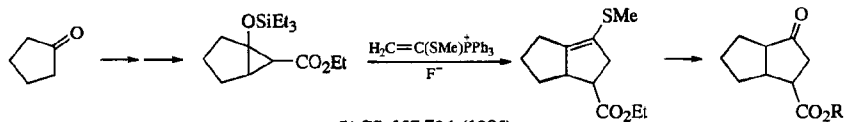
JACS 95 5311 (1973)

Acct Chem Res 7 85 (1974)

JOC 54 3334 (1989)

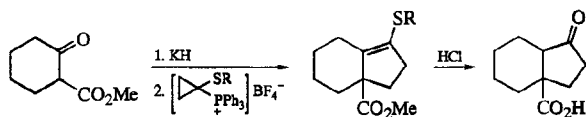


JACS 98 248 (1976)



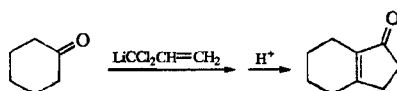
JACS 107 734 (1985)

JOC 52 1, 4139 (1987)



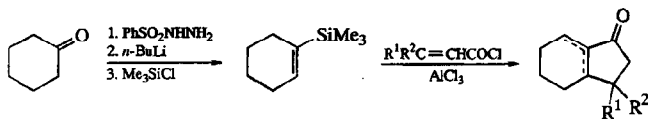
TL 4531 (1975)

JOC 46 1828 (1981)

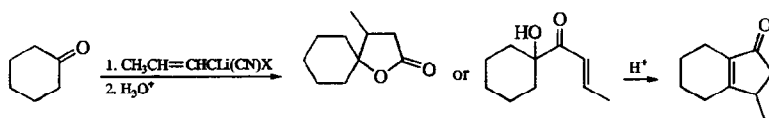


TL 771 (1978)

BCSJ 53 1010 (1980)



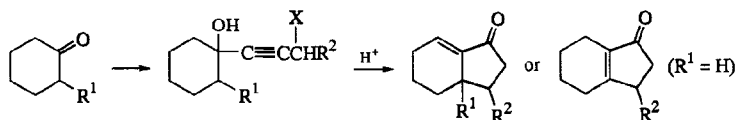
JOC 45 3017 (1980)

 \underline{X} NMe₂OCH(OEt)CH₃OSiMe₃

TL 21 1205 (1980)

JOC 45 395 (1980)

JOC 44 462 (1979); 45 395 (1980)

 \underline{X}

OH

Helv 59 1226 (1976)

JCS Perkin 1 410 (1976)

TL 3585 (1976); 3529 (1979); 3897 (1980)

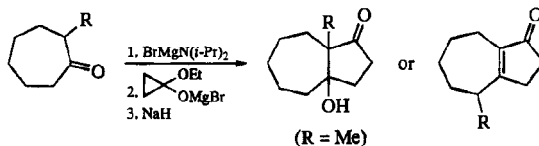
JACS 101 1599 (1979); 107 1769 (1985)

BCSJ 54 2747 (1981)

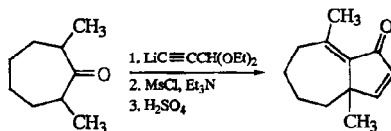
JOC 53 1441 (1988); 54 3449 (1989)

NEt₂

JCS 2247 (1953)



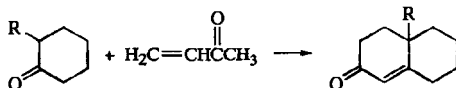
TL 30 6837 (1989)



TL 22 3565 (1981)

6. Four-Carbon Annulation

6.1. Robinson and Related Annulations



Reviews

Tetr 32 3 (1976)

Syn 177 (1976)

Stereochemistry

JOC 29 2501 (1964); 31 2543 (1966); 33 3913 (1968); 36 178, 594 (1971)

TL 4807 (1965)

CC 753 (1967); 47, 1249 (1968)

Can J Chem 47 4307 (1969)

JACS 93 1539 (1971)

Acid promotion

TL 4995 (1971)

JOC 45 5399 (1980)

JACS 108 4561 (1986)

Amino acid-catalyzed chiral annulation

Angew Int 10 496 (1971)

JOC 39 1612, 1615 (1974); 40 675 (1975)

Helv 60 2747 (1977)

JCS Perkin I 2349 (1983)

Org Syn 63 26, 37 (1984)

Tetr 40 1031 (1984)

TL 27 1501 (1986) (mechanism)

Org Syn Coll Vol 7 363 (1990)

Aprotic conditions

JOC 48 3349 (1983)

Use of enamines

JACS 92 5657 (1970)

JOC 40 862 (1975); 47 1438 (1982); 50 2607 (1985)

Tetr 32 1415 (1976)

Syn Commun 6 237 (1976)

Org Syn Coll Vol 6 496 (1988); 7 473 (1990)

Use of imines

JACS 107 273 (1985) (chiral)

TL 29 2787, 4427 (chiral) (1988)

Use of enol silanes

TL 31 1581 (1990)

Modified Michael acceptors and their equivalents

$\text{CH}_3\text{CH}(\text{OCH}_2\text{Ph})\text{CH}_2\text{CH}_2\text{Br}$

JACS 78 501 (1956)

$(\text{CH}_3\text{COCH}_2\text{CH}_2\text{NMeEt}_2)\text{I}$

JCS 1855 (1949)

$\text{CH}_3\text{COCH}_2\text{CH}_2\text{Cl}$

JCS 1029 (1964)

$\text{ClCH}_2\text{COCH}_2\text{CH}_2\text{Cl}$

CC 367 (1971)

$\text{CH}_3\text{OCH}_2\text{COCH}_2\text{CH}_2\text{OCH}_3$

JACS 100 1263, 2140, 2150 (1978)

$\text{RCH}_2\text{COC}(\text{SiMe}_3)=\text{CH}_2$

JACS 95 6152, 6867 (1973); 96 6179 (1974); 107 7184 (1985); 110 1985 (1988)

Org Syn 58 158 (1978)

CC 174 (1982)

Can J Chem 60 509 (1982)

Tetr 39 925 (1983)

Org Syn Coll Vol 6 666 (1988)

TL 30 5073 (1989)

$\text{CH}_3\text{COC}(\text{SPh})=\text{CH}_2$

JOC 47 1200 (1982)

$\text{CH}_3\text{O}_2\text{CCH}_2\text{COCH}=\text{CH}_2$

JACS 86 2034 (1964)

TL 2755 (1972)

$\text{CH}_3\text{CH}(\text{SePh})\text{COCH}=\text{CH}_2$

Syn Commun 8 211 (1978)

$n\text{-Bu}_3\text{SnCH}_2\text{CH}_2\text{COCH}=\text{CH}_2$

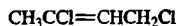
JACS 115 5934 (1993)

$\text{H}_2\text{C}=\text{CH}(\text{CH}_2)_3\text{COCH}=\text{CH}_2$
(bis-annulation)

JACS 101 5070 (1979)

$\text{CH}_3\text{C}(\text{SiMe}_3)=\text{CHCH}_2\text{I}$

JACS 96 3682, 3684 (1974)



Coll Czech Chem Commun 13 300 (1948)

Helv 32 1284, 2360 (1949)

BSCF 780 (1954)

JACS 82 4245 (1960)

JOC 30 3642 (1965); 57 4807 (1986)

Tetr 25 2159 (1969)

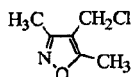
Acct Chem Res 5 311 (1972)

BCSJ 52 2978 (1979)

TL 29 4959 (1988)



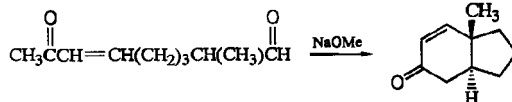
JOC 43 4673 (1978)



JACS 89 5459, 5463, 5464 (1967)

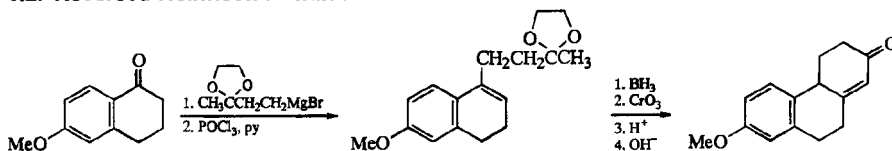
JOC 37 1652, 1659, 1664 (1972)

Org Syn Coll Vol 6 781 (1988)



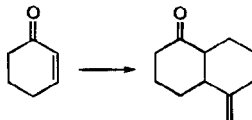
JACS 104 310, 3767 (1982)

6.2. Reversed Robinson Annulation



TL 3105 (1976)

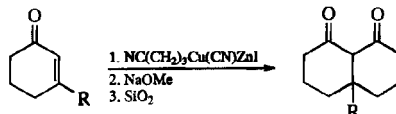
6.3. Other Four-Carbon Annulations



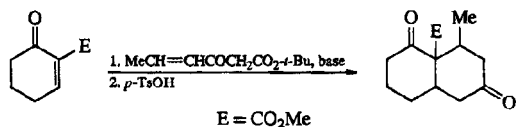
$\text{H}_2\text{C}=\text{C}(\text{MgBr})(\text{CH}_2)_3\text{Cl}$, $\text{CuBr} \cdot \text{SMe}_2$, $(\text{BF}_3 \cdot \text{OEt}_2)$ / JOC 49 4567 (1984)
 KH or KO-*t*-Bu CC 1342 (1987)

$\text{H}_2\text{C}=\text{C}(\text{CuCNLi})(\text{CH}_2)_3\text{Cl}$ / LDA

TL 32 5219 (1991)

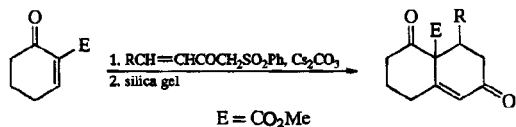


TL 29 6693 (1988)

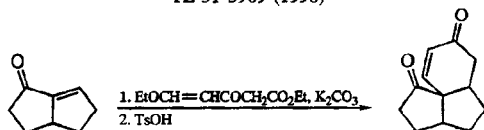


TL 29 5117 (1988); 31 3961 (1990)

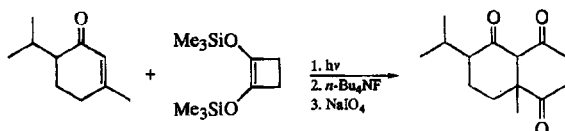
SL 516 (1990)



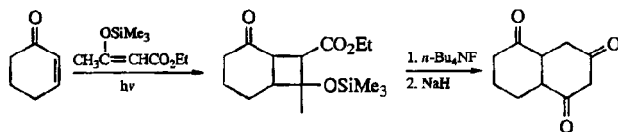
TL 31 3969 (1990)



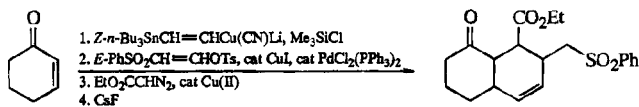
JACS 116 4689 (1994)



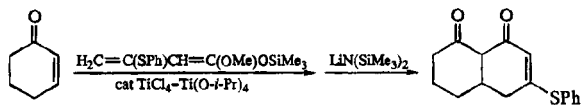
Syn 1024 (1980)



TL 23 295 (1982)

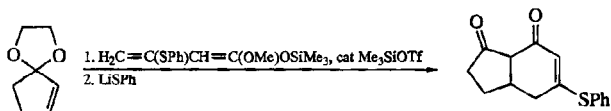


JACS 110 7916 (1988)

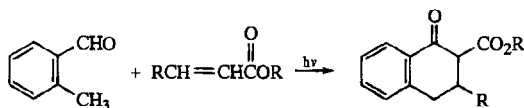


JOC 52 110 (1987); 59 6710 (1994)

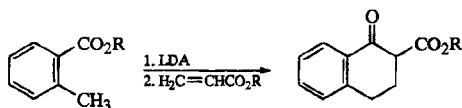
Can J Chem 68 1170 (1990)



JOC 54 3242 (1989)

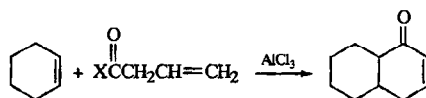


SL 51 (1991)



Syn 785 (1986)

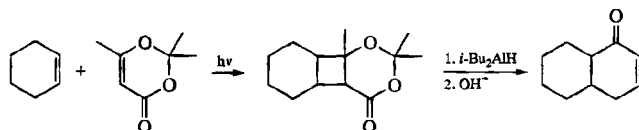
TL 30 3861 (1989)



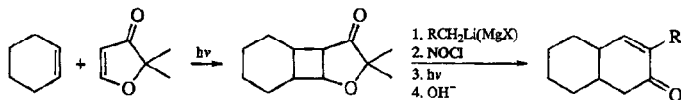
X = Cl, Br

CC 263 (1979)

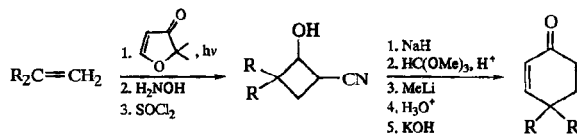
JOC 44 4042 (1979)



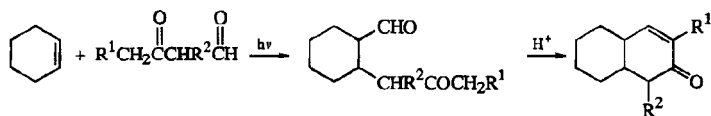
JACS 102 3634 (1980)



JACS 104 4990 (1982)

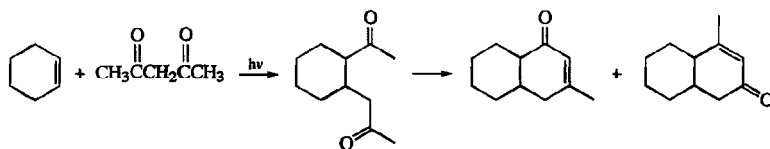


TL 2657 (1979); 23 1235 (1982)

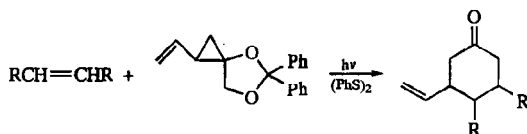


TL 3969 (1975)

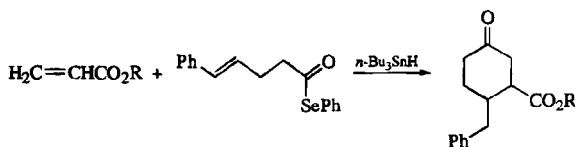
IOC 40 1865 (1975); 59 421 (1994)



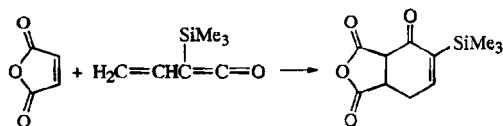
Can J Chem 41 440 (1963)



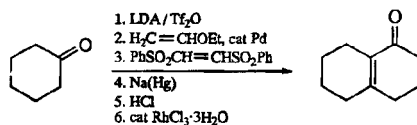
TL 31 823 (1990)



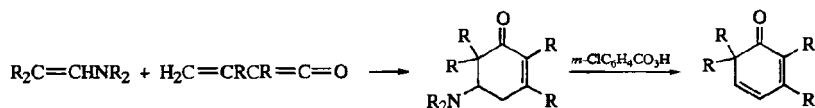
JACS 112 4003 (1990)



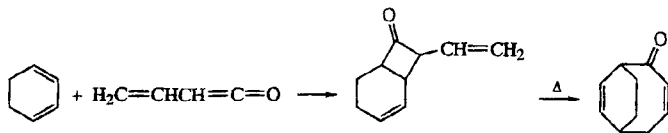
IOC 45 4810 (1980)



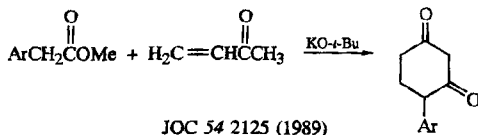
JOC 55 2443 (1990)



Helv 65 2230 (1982)

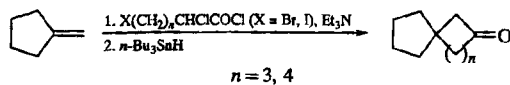


JACS 104 7670 (1982)

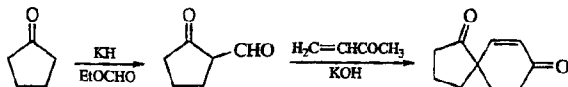


JOC 54 2125 (1989)

7. Four- and Five-Carbon Annulation

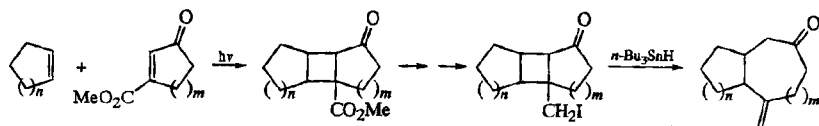
 $n = 3, 4$

TL 33 3285 (1992)



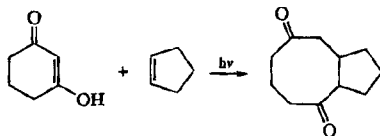
Syn 796 (1983)

8. Five- and Six-Carbon Annulation

 $n = 1, 2; m = 1, 2$

TL 31 5985 (1990)

9. Six-Carbon Annulation



TL 23 5485 (1982)

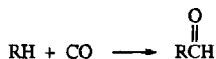
JOC 52 2905 (1987)

7. CARBONYLATION AND RELATED REACTIONS

Review: H. M. Colquhoun, D. J. Thompson, M. V. Twigg, "Carbonylation—Direct Synthesis of Carbonyl Compounds," Plenum, New York (1991)

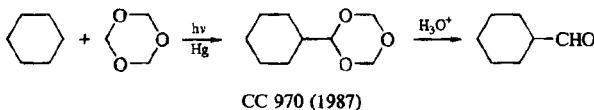
See also page 1381, Section 8.

1. Alkanes

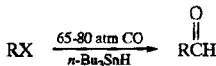


$h\nu$, cat $\text{ClRh}(\text{CO})(\text{PMe}_3)_2$ ($\text{R} = 1^\circ$ alkyl, aryl) JACS 112 7221 (1990)

$h\nu$, ArCOR ($\text{R} = 2^\circ$ alkyl) TL 33 2119 (1992)



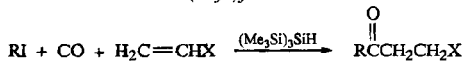
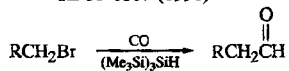
2. Free Radicals



$\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl, aryl; $\text{X} = \text{Br}, \text{I}$

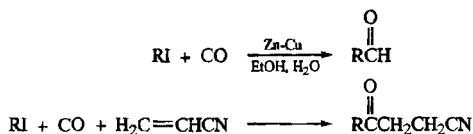
JACS 112 1295 (1990)

TL 31 6887 (1990)

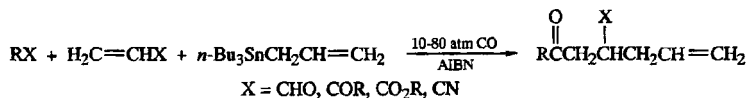


$\text{R} = 1^\circ$ alkyl, vinylic; $\text{X} = \text{CHO}, \text{COR}, \text{CO}_2\text{R}, \text{CN}$

SL 143 (1993); 643 (1994) (intramolecular)

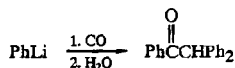


SL 1249 (1995)



JACS 115 1187 (1993)

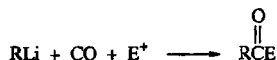
3. Organolithium Compounds



Org Prep Proc Int 13 144 (1981)



JOC 47 4347 (1982)



Review: Israel J Chem 24 167 (1984)

 E^+ $\text{Me}_3\text{SiCl} / \text{H}_2\text{O}$

JACS 104 5534 (1982)

 $\text{RCHO}, \text{R}_2\text{CO} / \text{H}_2\text{O}$

TL 24 4907 (1983)

JOC 48 1144 (1983); 57 5620 (1992); 58 5843 (1993)

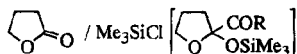
Org Syn Coll Vol 8 343 (1993)

 $\text{RCO}_2\text{R} / \text{H}_2\text{O}$

JOC 48 1144 (1983); 56 5768 (1991); 58 5843 (1993)

 $\text{RCOSR} / \text{H}_2\text{O}$

Organomet 3 327 (1984)



JOC 48 3367 (1983)

 $\text{COS} / \text{MeI} [\text{RCOCOSMe}]$

TL 25 2623 (1984)

 $\text{RNCO} / \text{H}_2\text{O}$

TL 25 5251 (1984)

 $\text{RNCS} / \text{H}_2\text{O}$

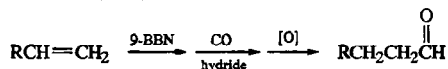
TL 25 5251 (1984)

 $\text{RN=C=NR} / \text{H}_2\text{O}$

JOC 50 1985 (1985)

4. Organoboron Compounds

Review: Acct Chem Res 2 65 (1969)

HydrideKHB(O-*i*-Pr)₃

CC 607 (1979); 1273 (1982)

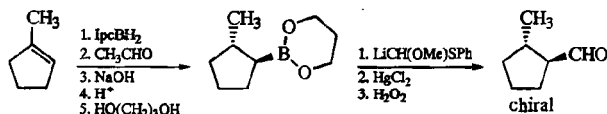
Syn 701 (1979)

TL 35 4751 (1994)

LiAlH(O-*t*-Bu)₃

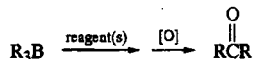
JACS 90 499 (1968); 91 2144, 4606 (1969)

JOC 59 406 (1994)



JACS 107 4980 (1985); 109 7553 (1987)

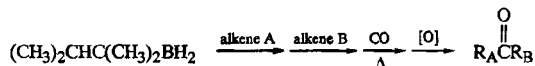
JOC 56 3286 (1991)

Reagent(s)CO, H₂O, Δ

JACS 89 2738, 4530 (1967)

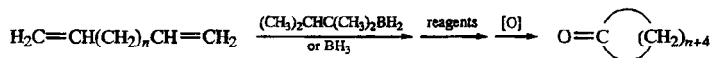
LiC(SPh)₃

CC 1149 (1981)



JACS 89 5285 (1967); 110 1529 (1988)

Syn 196 (1972)

Reagents

CO, Δ

JACS 89 5477 (1967); 115 11606 (1993)

CC 594 (1968); 607 (1979)

NaCN or KCN, (CF₃CO)₂O

TL 21 2381 (1980); 22 2075 (1981); 29 521 (1988);

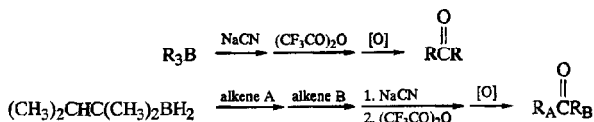
30 523 (1989)

Syn Commun 10 93 (1980)

CH₃OCHCl₂, KOEt₃

TL 30 2187 (1989)

JOC 54 2462 (1989)

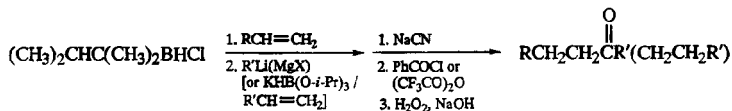


CC 1529 (1970); 1048 (1971); 186 (1973)

JCS Perkin I 129 (1975)

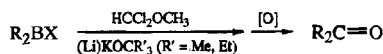
Syn Commun 10 675 (1980)

JACS 110 1529 (1988)



JACS 102 5919 (1980)

JOC 45 4542 (1980)



X = Cl, Br, OR

JACS 95 6876 (1973); 104 6844 (1982); 109 5420 (1987) (chiral)

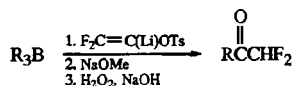
JOC 44 2417 (1979); 47 863 (1982); 53 1391 (1988) (chiral ynones); 56 3286 (1991)

Organomet 1 212 (1982)

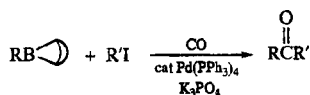
Tetr 40 1325 (1984) (chiral)

TL 28 3771 (1987)

SL 626 (1992) (2-alken-1-ones); 111 (1995)

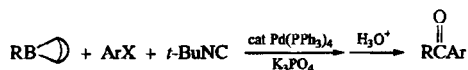


TL 30 5437 (1989)

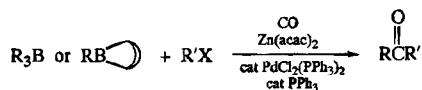


R' = 1°, 2°, 3° alkyl

TL 32 6923 (1991)

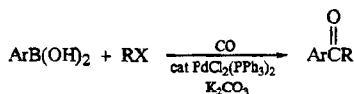


TL 33 4465 (1992)



R' = aryl, benzylic

JOMC 301 C17 (1986)

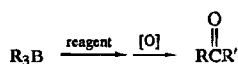


RX = ArOTf, ArI, PhCH₂Cl

TL 34 7595 (1993)

JOC 60 5899 (1995)

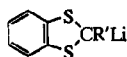
SL 147 (1995)



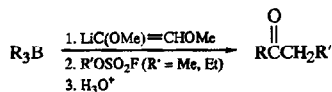
Reagent

LiCH(SPh)₂R'

CL 961 (1973)



TL 1893 (1979)



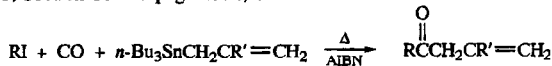
CL 1059 (1981)

5. Organosilicon Compounds

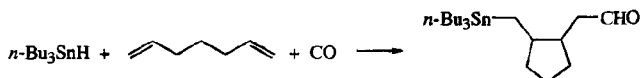
See page 1374, Section 17; page 1381, Section 1; and page 1389, Section 2.6.

6. Organotin Compounds

See also page 1373, Section 16 and page 1374, Section 17.



JACS 113 8558 (1991)



JOC 59 7570 (1994)

7. Organotitanium Compounds

Ti(O-*i*-Pr)₄, *i*-PrMgCl / CO

TL 36 4261 (1995)

Cp₂TiCl₂, 2 EtMgBr / CO

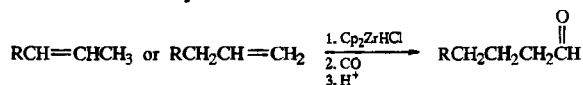
JOC 57 5803 (1992)

cat Cp₂Ti(PMe₃)₂, R₃SiCN / H₃O⁺

JACS 115 4912 (1993); 116 8593 (1994)

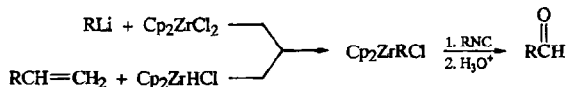
See also page 1368, Section 8; page 1369, Sections 9 and 10; page 1370, Section 12; page 1371, Section 14; and page 1373, Section 16.

8. Organozirconium Compounds

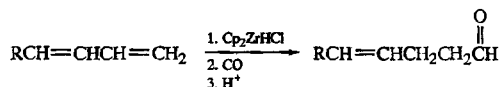


JACS 97 228 (1975)

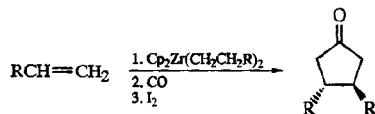
JOC 55 4688 (1990)



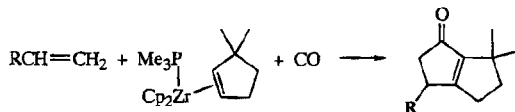
TL 29 1631 (1988)



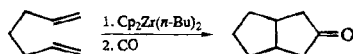
JACS 98 262 (1976)



JOC 54 3521 (1989)

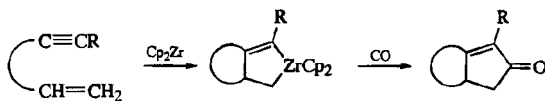


JACS 111 9113 (1989)



TL 30 5105 (1989)

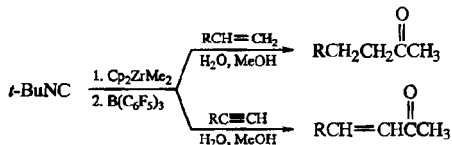
JOC 57 3519 (1992); 59 4993, 5633 (1994)



JACS 107 2568 (1985); 111 3336 (1989); 113 7424 (1991)

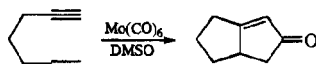
TL 27 2829 (1986); 28 917 (1987); 31 3691 (1990); 33 1543 (1992)

See also page 1368, Section 7; page 1369, Sections 9 and 10; page 1370, Section 12; page 1371, Section 14; and page 1373, Section 16.



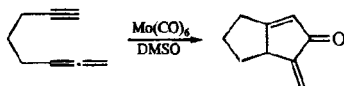
JOC 58 5595 (1993)

9. Organomolybdenum Compounds



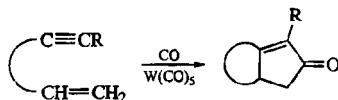
TL 34 4027 (1993)

See also page 1368, Sections 7 and 8; page 1369, Section 10; page 1370, Section 12; page 1371, Section 14; and page 1373, Section 16.



TL 36 2407 (1995)

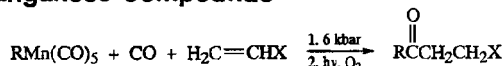
10. Organotungsten Compounds



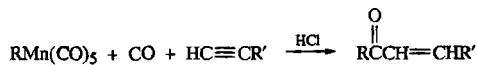
JACS 115 1154 (1993)

See also page 1368, Sections 7 and 8; page 1369, Section 9; page 1370, Section 12; page 1371, Section 14; and page 1373, Section 16.

11. Organomanganese Compounds

X = CO₂Me, SO₂Ph

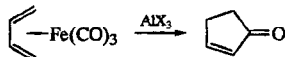
TL 28 2229 (1987)



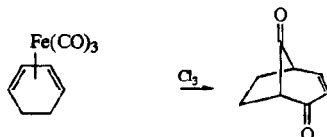
TL 28 2233 (1987)

12. Organoiron Compounds

See also page 712, Section 3.

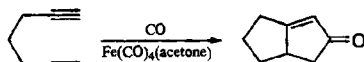


TL 33 7361, 7365 (1992)



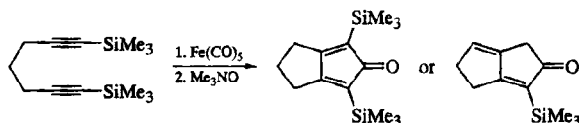
Ber 119 169 (1986)

SL 663 (1990)



CC 202 (1991)

See page 1368, Sections 7 and 8; page 1369, Sections 9 and 10; page 1371, Section 14; and page 1373, Section 16.



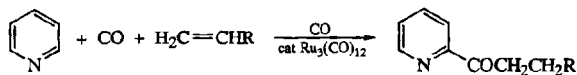
CC 426 (1982)

JCS Perkin I 2749 (1987)

Organomet 11 4096 (1992); 13 578 (1994)

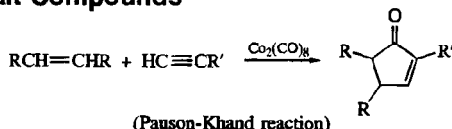
SL 924 (1993)

13. Organoruthenium Compounds



JACS 114 5888 (1992)

14. Organocobalt Compounds



See also page 1368, Sections 7 and 8; page 1369, Sections 9 and 10; page 1370, Section 12; and page 1373, Section 16.

Reviews:

Ann NY Acad Sci 295 2 (1977)

Tetr 41 5855 (1985)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 9.1, p 1037

Org Rxns 40 1 (1991)

Intermolecular:

JCS Perkin I 977 (1973); 30 (1976)

J Chem Res (S) 8 (1977); 244 (1983); 344, 3131 (1984)

Organomet I 1560 (1982)

TL 24 2905 (1983); 29 999 (1988); 30 595, 4021, 5865 (1989); 31 635 (1990); 32 151 (1992); 34 2087 (1993); 35 575 (1994) (chiral); 36 2867 (1995)

Tetr 41 5995 (1985)

JOC 50 5215 (1985); 52 3595 (1987); 53 203 (1988); 54 5662 (1989); 56 7048 (1991); 57 5106, 5277 (1992); 58 1659 (1993); 60 6670 (1995) (chiral)

JACS 110 968 (1988) (regiochemistry); 112 441 (1990) (polymer support); 113 1693 (1991); 116 2155 (chiral), 2163 (1994)

SL 20, 204 (1991); 577, 1083, 1085 (chiral) (1995)

Intramolecular:

JOC 46 5357, 5436 (1981); 49 5025 (1984); 52 569, 5296 (1987); 54 5148 (1989); 57 5277, 6853 (1992); 58 1659 (1993); 59 1396, 6968 (1994); 60 6912 (1995)

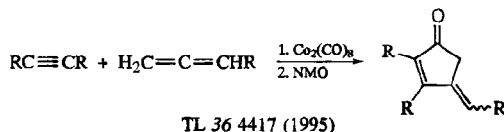
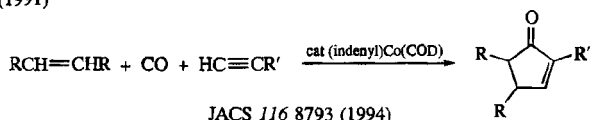
JACS 105 2477 (1983); 108 3128, 3835 (1986); 109 7495 (1987); 110 5224 (1988); 112 9388 (1990); 114 5555 (1992); 115 7199 (1993); 116 3159 (1994) (catalytic)

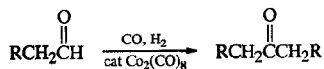
TL 25 4041 (1984); 26 2475, 4851 (1985); 27 1241, 1245 (1986); 28 5465 (1987); 31 5289, 7505 (1990); 32 2105, 2109, 2137, 6285 (1991); 33 3829 (1992); 34 3435, 4023 (1993); 35 1153, 3517, 3521, 4511, 5059, 8581 (1994); 36 4651, 5761 (chiral) (1995)

Bull Acad Sci USSR, Div Chem Sci 2434 (1984); 2455 (1985); 211, 213 (1987)

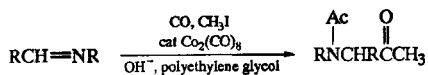
Tetr 41 5861 (1985)

SL 204 (1991)

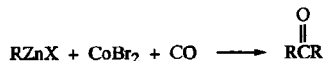




TL 31 3117 (1990)

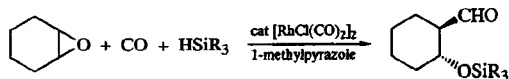


TL 29 5113 (1988)

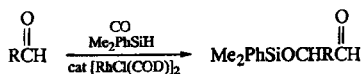


TL 36 8411 (1995)

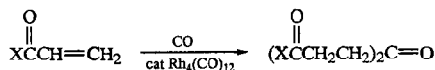
15. Organorhodium Compounds



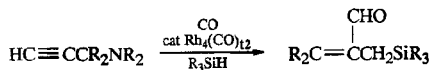
JOC 58 4187 (1993)



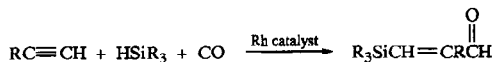
JACS 115 2059 (1993)

X = OR, NR₂

CL 361 (1982)



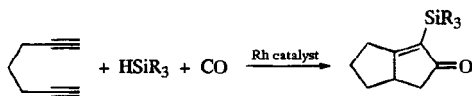
TL 33 5799 (1992)



JACS 111 2332 (1989); 117 4419, 6797 (1995) (both intramolecular)

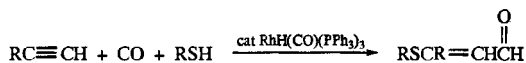
Organomet 10 38 (1991); 12 11 (1993)

TL 34 915 (1993); 36 8723 (1995)

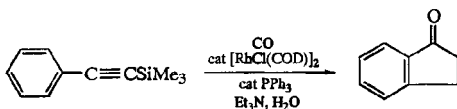


JOC 59 7594 (1994)

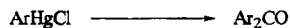
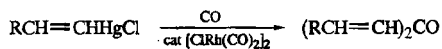
TL 36 241 (1995)



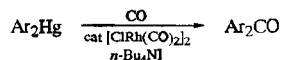
JACS 117 7564 (1995)



JOC 58 5386 (1993)



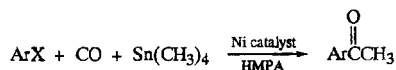
JOC 45 3840 (1980)



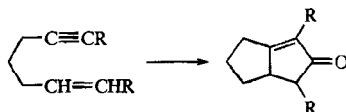
Bull Acad Sci USSR, Div Chem Sci 31 211 (1982)

16. Organonickel Compounds

See also page 1374, Section 17.



Syn 47 (1981)

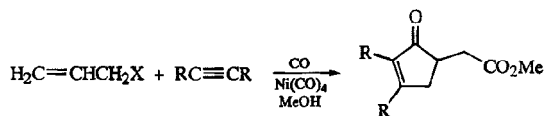
 Ni(CO)_4

TL 28 4745 (1987)

 Ni(COD)_2 , RNC, $n\text{-Bu}_3\text{P/H}_3\text{O}^+$

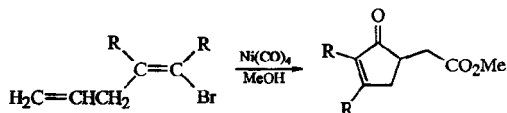
JACS 110 1286 (1988)

See also page 1368, Sections 7 and 8; page 1369, Sections 9 and 10; page 1370, Section 12;
and page 1371, Section 14.

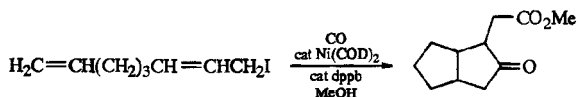


Acct Chem Res 6 422 (1973)

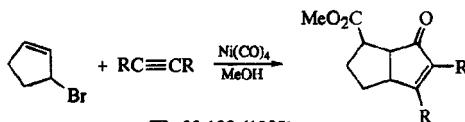
JOC 54 1969 (1989)



TL 29 5811 (1988)

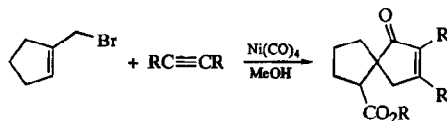


TL 31 1265 (1990)



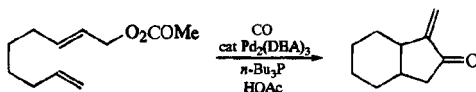
TL 33 109 (1992)

JACS 114 10449 (1992)

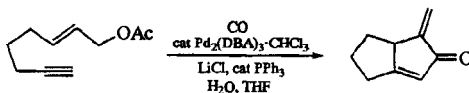


TL 33 113 (1992)

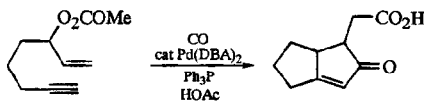
17. Organopalladium Compounds



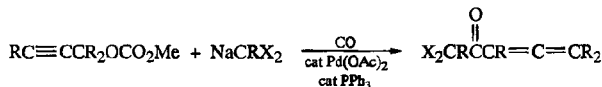
JACS 113 9660 (1991)



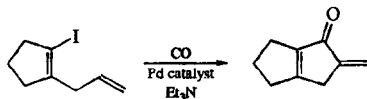
JOC 58 560 (1993)



Helv 74 465 (1991)

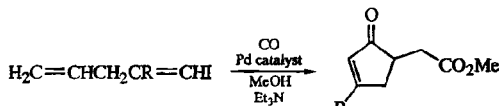

 X = COR, CO₂R

SL 697 (1991)



JOC 53 913 (1988)

TL 35 7939 (1994)



JACS 107 8289 (1985)

JOC 53 913 (1988)


 CO, cat PdCl₂, H₂, py (R = aryl)

BCSJ 49 1681 (1976)

 CO, cat PdX₂(PPh₃)₂ (X = Br, I), H₂, R₃N (R = aryl, heterocyclic, vinylic)

JACS 96 7761 (1974)

 CO, cat Pd(PPh₃)₄, NaO₂CH or Me₃Si(OSiHMe)_nOSiMe₃ (R = aryl)

JOC 49 4009 (1984)

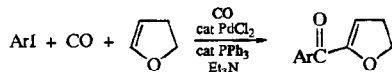
 CO, cat Pd(PPh₃)₄, *n*-Bu₃SnH (R = aryl, allylic, benzylic, vinylic; X = halide, OTf)

JACS 105 7175 (1983); 108 452 (1986)

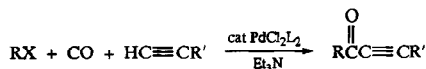
JOC 57 5979 (1992); 59 406 (1994)

TL 35 1833, 6993 (1994)

SL 313 (1995)

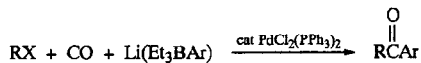


JOC 60 7267 (1995)



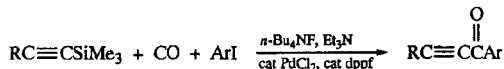
CC 333 (1981)

SL 823 (1995)

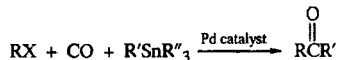


RX = aryl iodide, vinylic iodide or triflate

JOC 59 2634 (1994)



SL 823 (1995)



R = allylic, aryl, benzylic, vinylic; X = halide, OTf; R' = alkyl, allylic, aryl, vinylic, heterocyclic

TL 2601 (1979); 29 1173 (1988)

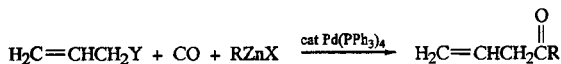
JOMC 205 C27 (1981)

JACS 105 7173 (1983); 106 4833, 6417, 7500 (1984); 110 1557 (1988); 112 8465 (1990) (intramolecular);
113 4903 (1991); 115 3966, 9293 (1993); 117 5776, 8474 (1995)

Organomet 3 1108 (1984)

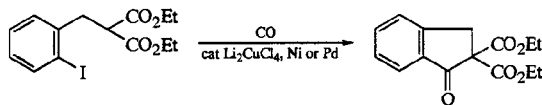
JOC 54 3334 (1989); 55 3114 (1990); 57 1262 (1992); 60 8341 (1995)

Org Syn Coll Vol 8 97 (1993)

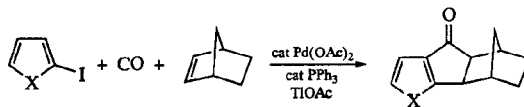


Y = O₂CPh, OPO(OEt)₂

JOC 60 1365 (1995)

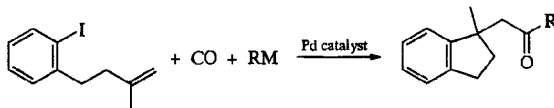


JACS 111 8018 (1989)



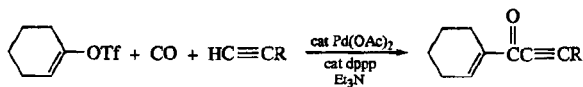
X = O, S

TL 35 3197 (1994)

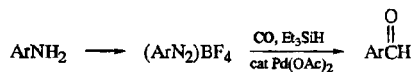


RM = NaBPh₄, *n*-Bu₃SnR

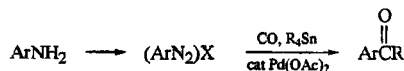
TL 35 4429 (1994)



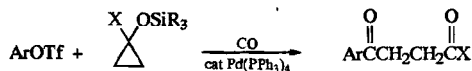
TL 32 6449 (1991)



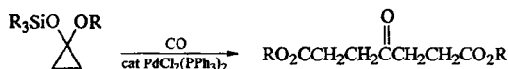
JOMC 270 283 (1984)


 $\text{X} = \text{BF}_4, \text{PF}_6$

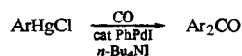
CL 35 (1982)


 $\text{X} = \text{alkyl, aryl, OR}$

SL 741 (1990)

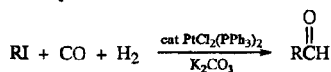


TL 29 1541 (1988)



Bull Acad Sci USSR, Div Chem Sci 31 211 (1982)

18. Organoplatinum Compounds


 $\text{R} = 1^\circ, 2^\circ \text{ alkyl}$

CC 351 (1986)

JOC 54 1831 (1989)

19. Organocopper Compounds

See page 1374, Section 17.

20. Organomercury Compounds

See page 1372, Section 15, and page 1374, Section 17.

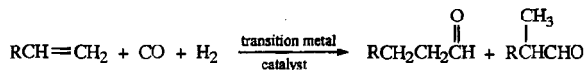
21. Organosamarium Compounds



JOC 56 1 (1991)

22. Hydroformylation, Hydroacylation and Related Reactions

See also page 1329, Section 1.



Reviews:

J. Falbe, "Carbon Monoxide in Organic Synthesis," Springer, New York (1970)

Catal Rev 6 49 (1972)

"Organic Synthesis via Metal Carbonyls," Eds. I. Wender and P. Pino, J. Wiley, New York (1977)

J Mol Catal 4 243 (1978)

Topics Curr Chem 105 77 (1982) (chiral)

J. A. Davies, "The Chemistry of the Metal-Carbon Bond," Eds. F. R. Hartley and S. Patai, J. Wiley, New York (1985), Vol 3, Chpt 8

J Chem Ed 63 196 (1986)

JACS 109 7714 (1987) (fluoroalkenes)

Chirality 3 355 (1991)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Part 4.5, p 913

Chem Rev 95 2485 (1995) (asymmetric)

Metal

Ru

Adv Organometal Chem 32 121 (1991)

Co

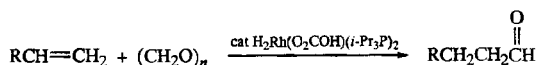
JACS 99 1058 (1977); 103 7590, 7594 (1981)
JOC 59 3091 (1994)

Rh

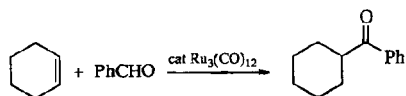
JACS 95 6504 (1973); 99 1058 (1977); 112 3674 (1990); 115 2066, 7033 (chiral) (1993)
BCSJ 47 1698 (1974) (chiral)
Org Syn 57 11 (1977)

Angew Int 19 178 (1980) (review); 33 67 (1994)
 JOC 46 4422 (1981) (chiral); 53 4422 (1988); 54
 5208 (1989); 55 2138 (1990); 57 3729 (1992); 58
 3326 (1993); 59 3091, 7125 (1994); 60 499, 6612,
 7078 (1995)
 JOMC 279 193 (1985) (chiral)
 R. S. Dickson, "Homogeneous Catalysis with
 Compounds of Rhodium and Iridium," Reidel,
 Dordrecht (1985), pp 139-158
 Org Syn Coll Vol 6 338 (1988)
 TL 30 5357 (1989); 31 2461 (1990); 35 2023, 4295
 (1994) (both chiral)
 SL 711 (1990); 615 (1994); 519 (1995)

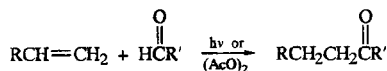
Ir JOC 59 3091 (1994)
 Pd JOC 51 4189 (1986) (chiral)
 Pt JACS 97 3553 (1975); 109 7122 (1987) (chiral)
 J Catalysis 45 256 (1976)
 Helv 59 642 (1976) (chiral)
 CL 361 (1978) (chiral)
 JOMC 213 503 (1981); 279 193 (1985) (chiral); 296
 281 (1985) (chiral)
 Helv 64 1865 (1981)
 TL 29 1911 (1988) (chiral); 30 5759 (1989)
 Organomet 10 1183, 2046 (1991) (both chiral)



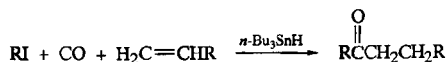
TL 23 4967 (1982)



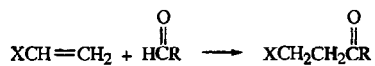
TL 28 6229 (1987)
 JOC 55 1286 (1990)



JOC 14 250 (1949)

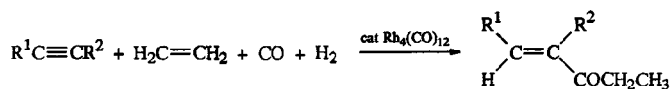


JOC 56 5003 (1991)

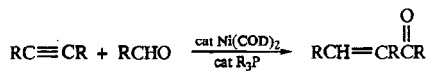


X = COR, CO₂R, CN, etc.

See conjugate addition under the appropriate functional group X.



CL 401 (1982)



JOC 55 2554 (1990)

8. ELECTROPHILIC ACYLATION

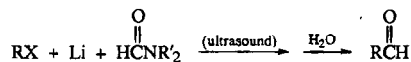
1. Synthesis of Aldehydes

Reviews:

Quart Rev 20 179 (1966)

Heterocycles 6 731 (1977)

Chem Rev 87 671 (1987)



R = 1°, 2°, 3° alkyl; benzylic; aryl

Syn 160 (1973)

TL 23 3361 (1982); 27 1791 (1986); 30 5563 (1989)



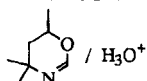
M

Reagents

Li

CNC(CH₃)₂C(CH₃)₃ / H₃O⁺

JACS 91 7778 (1969); 92 6675 (1970)



TL 5151 (1969)

PhMeNCHO / H₃O⁺

JOC 59 7701 (1994)

Li (BF₃·OEt₂)

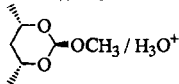
HCONMe₂ / H₃O⁺

JOC 58 5690 (1993) (R = C≡CR)

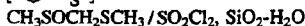
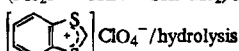
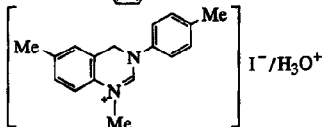
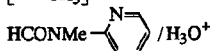
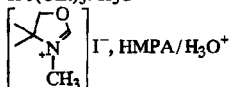
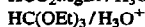
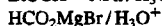
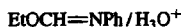
MgX

Fe(CO)₅ / H₃O⁺

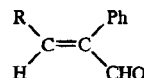
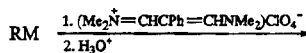
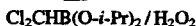
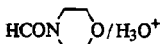
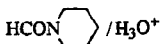
BCSJ 55 1663 (1982)



JACS 92 584 (1970)

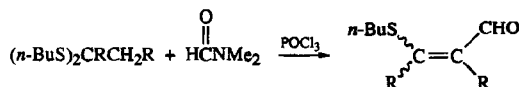
**M****Reagents**

Li or MgX



R = 1° alkyl, benzylic, aryl; M = Li, MgX

Syn Commun 11 561 (1981)



TL 35 2585 (1994)

JOC 6 489 (1941); 54 6120 (1989)

TL 21 2869 (1980)

JOC 6 437 (1941)

JACS 92 6676 (1970)

Angew Int 15 270 (1976)

Org Syn Coll Vol 6 64 (1988)

Syn 403 (1978)

TL 5179 (1978)

JACS 77 5118 (1955)

Syn Commun 11 571 (1981)

JCS Perkin I 1886 (1976)

TL 22 1821 (1981)

TL 3883 (1977)

JOC 6 437 (1941); 51 3762, 5106 (1986);
58 4132 (1993)JCS 3334 (1955); 4691 (1956); 1054
(1958)

Chem Ind 1596 (1957)

Compt Rend 275 511 (1972)

Syn 160 (1973)

JACS 114 9369 (1992)

Angew Int 20 878 (1981)

Org Syn 64 114 (1985)

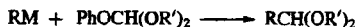
JOC 50 2423, 2427 (1985); 51 142 (1986);
52 5560 (1987)

TL 29 6775 (1988)

Org Syn Coll Vol 7 451 (1990)

JOC 49 3856 (1984)

JOMC 122 145 (1976)

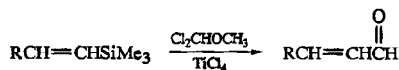
RM

RMgX (R = 1°, 2° alkyl; aryl; alkynyl; propargylic; vinyl)
 Ber 103 643 (1970)
 Syn 379 (1975)

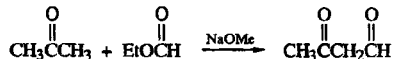
J Chem Res (S) 343 (1981)

RCH=CHCH₂M (M = MgX, ZnX, Al_{2/3}Br) J Chem Res (S) 343 (1981)

RCH=C=CHCH₂Al_{2/3}Br J Chem Res (S) 343 (1981)



CL 859 (1978)

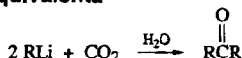


Org Syn Coll Vol 4 210 (1963)

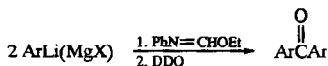
2. Synthesis of Ketones

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 1, Part 1.13, p 397

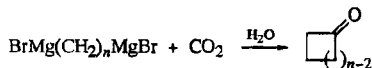
2.1. From Carbonyl Cation Equivalents



JACS 55 1258 (1933); 75 1771 (1953); 77 2806 (1955)



JOC 54 6120 (1989)



$\frac{n}{2}$

3

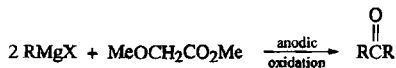
Syn 721 (1983)

4

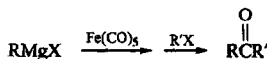
Ber 44 1918 (1911)

5

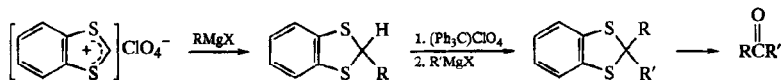
Compt Rend 144 1358 (1907)



TL 3625 (1977)

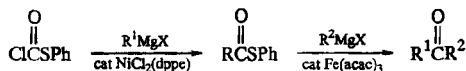


TL 761 (1978)



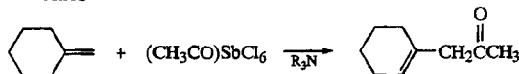
JCS Perkin I 1886 (1976)

TL 22 1821 (1981)



TL 26 3595 (1985); 29 3587 (1988)

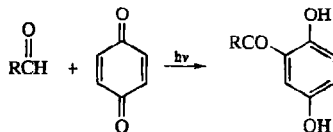
2.2. From Acylium Salts



IACS 99 6008 (1977)

2.3. From Aldehydes

See page 1435, Section 9, and page 1451, Section 10, for related reactions.



JOC 57 3256 (1992)

TL 35 7723 (1994)

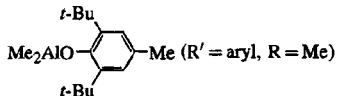


RMgX/PhCHO

TL 28 769 (1987)

RCHB(mesityl)₂/(CF₃CO)₂O or NCS (R = CH₂R)

TL 30 5643 (1989)



TL 31 323 (1990)

Me₃SiCBr₃, CrBr₃-LiAlH₄ (R = Me)

SL 663 (1994)

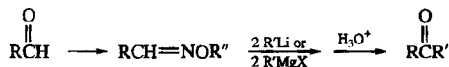
Cp₂ZrRCl (R = 1° alkyl, vinylic)/PhCHO

JOC 60 3278 (1995)

RVCl₂ (R = alkyl, alkynyl, aryl, vinylic)

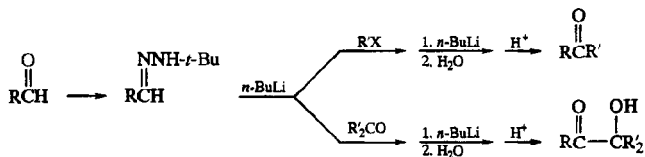
IACS 107 7179 (1985)

TL 27 933 (1986)



R = aryl > alkyl

TL 27 3033 (1986)



CC 1040 (1983)

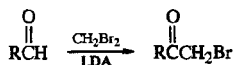
X,Y

H, F

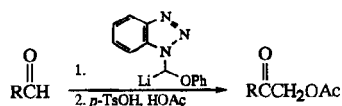
TL 24 725 (1983); 35 4851 (1994)

Cl, Cl

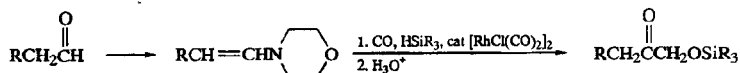
TL 24 527 (1983)



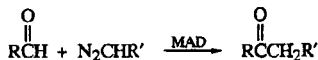
TL 31 3669 (1990)



TL 36 841 (1995)



JOC 57 2 (1992)



SL 521 (1994)

XCatalyst

COR

SnCl₂

JOC 55 5297 (1990)

COCO₂RSnCl₂

SL 705 (1991)

CO₂RBF₃·OEt₂

JOC 54 3258 (1989)

GeCl₂

JOC 54 3258 (1989)

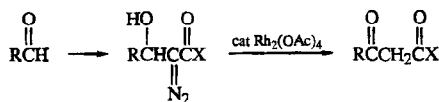
SnCl₂

JOC 54 3258 (1989); 57 2732 (1992); 58 1762 (1993); 59 488 (1994)

XCatalyst

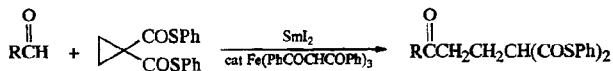
TiCl ₄	JOC 59 488 (1993)
ZrCl ₄	TL 34 2183 (1993)
	JOC 59 488 (1993)
SnCl ₂	TL 33 1131 (1992)
SnCl ₂	TL 33 1131 (1992)
SnCl ₂	TL 33 1131 (1992)

See also page 1311, Section 10.

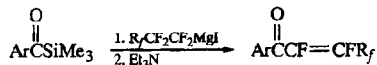
X = R, OR, NR₂

CC 959 (1979)
 JCS Perkin I 2566 (1981)
 IACS 109 6187 (1987)
 TL 29 4481 (1988)
 JOC 55 4144 (1990)

See also page 1311, Section 10.



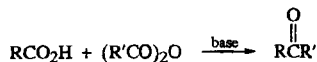
TL 35 7805 (1994)

2.4. From Acylsilanes

TL 32 83 (1991)
 JOC 58 6671 (1993)

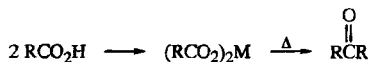
2.5. From Carboxylic Acids

See also page 1422, Section 3.



Dakin-West reaction

J Biol Chem 78 91, 745, 757 (1928)
 JOC 50 1112 (1985)
 Chem Soc Rev 17 91 (1988) (review)
 TL 36 4797 (1995)

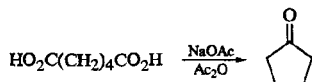
M

Mg

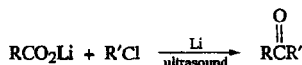
Org Syn Coll Vol 4 854 (1963)

Ba

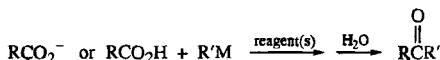
Org Syn Coll Vol 1 192 (1941)



JOC 58 4555 (1993)



SL 459 (1995)

MReagent(s)

Li

—

JCS 2012 (1950)

Acta Chem Scand 6 782 (1952)

JOC 33 943 (1968); 40 1770 (1975); 41 1176

(1976); 48 2260, 4789 (1983); 50 325 (1985); 51

2361 (1986); 52 4171, 5501 (1987); 54 1866

(1989); 56 2499, 3102, 4341 (1991); 58 1372,

4191, 4758 (1993)

JACS 91 456 (1969); 92 2590 (1970); 95 4873

(1973); 100 1600 (1978); 103 6157 (1981); 106

1095, 2064, 6702 (1984); 107 996, 5717, 7546

(1985); 108 1617, 4484 (1986); 109 3025 (1987);

110 4652, 7447 (1988); 111 6717 (1989)

Org Rxs 18 1 (1970) (review)

Org Syn Coll Vol 5 775 (1973)

TL 2877 (1974); 28 4965 (1987); 36 881 (1995)

Syn Commun 11 7 (1981)

TL 35 203 (1994)

CeCl₃

MgX

—

JACS 78 2268 (1956) (perfluorinated acids); 106

1095 (1984); 108 7727 (1986) (LiO₂CCF₃)

Austral J Chem 30 427 (1977); 35 1739 (1982)

(R'M = H₂C=CHMgBr)

JOC 48 2260 (1983); 50 325 (1985); 52 3474

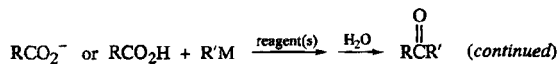
(1987); 54 1866 (1989)

TL 36 1791 (1995)

TL 24 3677 (1983)

NiCl₂(dppe)[p-MeOC₆H₄CCl=N⁺Ph₂]⁺Cl⁻

TL 23 5059 (1982)

MReagent(s) Ph_2POCl , Et_3N

Syn Commun 8 59 (1978)

CC 412 (1986)

 $\text{Me}_2\text{C}=\text{C}(\text{Cl})\text{NR}_2$, cat CuI

CL 1791 (1983)

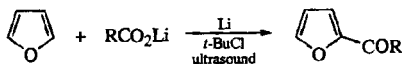
Org Syn Coll Vol 8 441 (1993)

 CeX_2

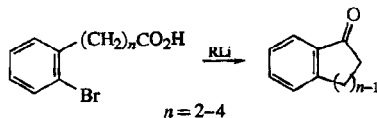
—

JOC 59 3142 (1994)

TL 35 203 (1994)



JOC 60 8 (1995)

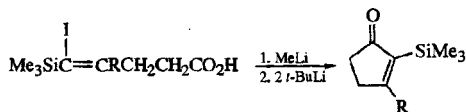


JOC 40 2394 (1975)

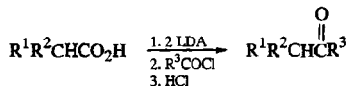
JACS 99 4822 (1977)

TL 28 2933 (1987)

SL 95 (1991)



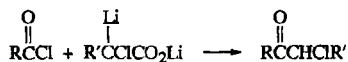
JACS 105 6761 (1983)



JOC 42 1189 (1977)

Compt Rend 286 401 (1978)

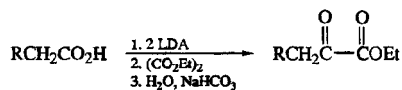
Syn 284 (1982)



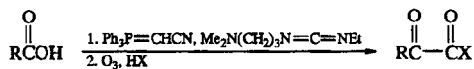
Syn 284 (1982)



See page 1528, Section 22, for this and related reactions.

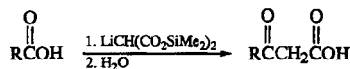


TL 22 2439 (1981)



X = OH, OR, NHR

JOC 59 4364 (1994)



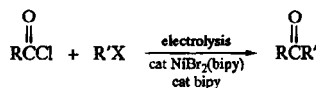
See page 1528, Section 22, for this and related reactions.



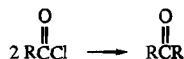
See page 1528, Section 22, for this and related reactions.

2.6. From Acid Halides

See also page 1422, Section 3.



JOMC 369 C47 (1989)

Et₃N/H₂O, Δ

JACS 69 2444 (1947)

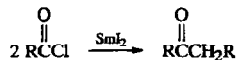
Org Syn Coll Vol 4 555, 560 (1963)

Fe₂(CO)₉

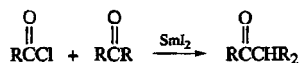
TL 3861 (1977)

electrolysis

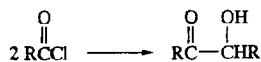
TL 34 7571 (1993)



TL 30 7407 (1989)

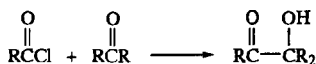


TL 30 7407 (1989)



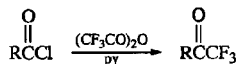
SmI₂ JOC 56 3118 (1991)
TL 35 1723 (1994)

SmCp₂ JOC 56 3118 (1991)



SmI₂ TL 25 2869 (1984); 33 2621 (1992); 35 1723 (1994)
JOC 56 3118 (1991)

SmCp₂ JOC 56 3118 (1991)



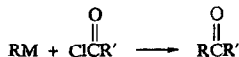
TL 33 1285 (1992)



Li, ultrasound TL 22 2757 (1981)

SmI₂ TL 22 3959 (1981); 25 2869 (1984)
JOC 56 3118 (1991)

SmCp₂ JOC 56 3118 (1991)



Reviews: Org Rxs 8 28 (1954) (Mg, Zn, Cd); 22 253 (1975) (Cu)

RM

RLi, cat CuX (X = Cl, I) (R = 1°, 2°, 3° alkyl) TL 829 (1971)

LiCH₂CO₂SiMe₃ (R = Me after H₃O⁺, Δ) Syn Commun 13 183 (1983)

Li₂CHSO₂Ph JOC 53 906 (1988)

ArLi, cat Fe(acac)₃ JOC 53 4978 (1988)

o-LiC₆H₄CO₂Li JOC 46 1057 (1981)

RC≡CLi, BF₃·OEt₂ TL 29 2279 (1988)




RC≡CLi, cat CuCl JOC 58 3516 (1993)

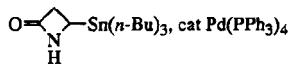
RMgX Org Syn Coll Vol 6 991 (1988)

RMgX, THF, -78 °C (R = 1°, 2°, 3° alkyl; allylic; aryl) TL 4303 (1979); 21 2303 (1980); 36 2757 (1995)
Ber 114 2479 (1981)
JOC USSR 18 859 (1982)
CL 13 (1986)

	JOC 54 2183 (1989); 55 1114 (1990); 57 3535 (1992)
RMgX, HMPA (R = 1°, 2° alkyl; aryl; alkynyl; vinylic)	Compt Rend C 275 511 (1972)
RMgBr, VCl ₃ (R = 1° alkyl, aryl)	TL 27 929 (1986)
RMgX, cat Li ₂ MnCl ₄ (R = 1°, 2° alkyl; aryl; vinylic)	TL 33 4439 (1992)
RMgX, FeCl ₃ (R = 1°, 3° alkyl)	JACS 75 3731 (1953) JOC 26 1768, 1772 (1961)
RMgX, cat Fe(acac) ₃ (R = 1°, 2°, 3° alkyl; aryl)	TL 25 4805 (1984); 26 1285 (1985); 28 2053 (1987) JOC 53 4978 (1988)
RMgX, cat CuX (X = Cl, I) (R = 1°, 3° alkyl)	JACS 71 4141 (1949); 75 3731 (1953) TL 829 (1971); 467 (1972) Tetr 29 3943 (1973); 37 4189 (1981) J Chem Res (S) 46 (1978) JOC 53 4555 (1988); 57 1047 (1992)
RMgX, cat Cu-CuCl (R = 1°, 3° alkyl)	TL 2523 (1970)
RMgX, CuCl (R = 1° alkyl)	BSCF II 318 (1982)
RMgX, CuI (R = 3° alkyl)	JOC 59 2594 (1994)
NaCo(I)Salen/MeMgI/H ₃ O ⁺	Tetr 37 863 (1981)
RCaX, CuCN·2LiBr	JOC 55 5045 (1990)
F ₂ C=CRBR ₂ , CuI	TL 33 337 (1992) JOC 60 2320 (1995)
R ₄ BLi (R = 1° alkyl, benzylic)	JOC 40 1676 (1975)
(R ₃ BMe)Li, CuCl·COD (R = 1° alkyl)	TL 173 (1977)
RAIAlCl ₂ (R = 1° alkyl)	JACS 108 6036 (1986)
R ₃ Al, Cu(acac) ₂ , PPh ₃ (R = 1° alkyl)	BCSJ 54 1281 (1981)
(R ₄ Al)Li, cat CuCl (R = 1° alkyl)	CL 623 (1979)
(R ₄ Ga)Li or (R ₃ GaR)Li (R = 1° alkyl, PhCH ₂ , Ph, C≡CR)	TL 36 1287 (1995)
R ₃ Tl (R = Me, Et, Ph)	JOC 55 3368 (1990)
Me ₂ TiC≡CR	IOC 55 3368 (1990)
R ₄ Si, AlCl ₃ (R = 1° alkyl)	Syn 677 (1977)
RSiMe ₃ , AlCl ₃ (R = 1° alkyl)	JOC 49 1140 (1984) Org Syn Coll Vol 8 486 (1993) (both intramolecular)
ArSiMe ₃ , AlCl ₃	SL 817 (1995) TL 36 881 (1995)

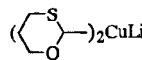
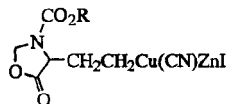
RM

- ArSiMe₃**, cat KO-*t*-Bu (on R'COF) *Angew Int* 20 265 (1981)
- RSiR'₃**, ZnCl₂ (R = 2-thienyl, 2-furyl) *JOC* 47 3219 (1982)
- H₂C=CHCH₂CH₂SiMe₃**, TiCl₄ (R = ) *TL* 4045 (1977)
- CH₂SiMe₃, AlCl₃ (R = CH₂CH₂CH=CH₂) *Can J Chem* 59 802 (1981)
- , AlCl₃ (R = CH₂CH=CHCH₃) *TL* 22 2883 (1981)
- R₂C=CRCH₂SiMe₃** *TL* 35 3727 (1994)
- RSiR'₃**; EtAlCl₂, AlCl₃, TiCl₄ or ZnCl₂ (R = allylic) *JOMC* 85 149 (1975)
TL 1871 (1976); 1385 (1977); 429 (1979); 21 831, 3783, 4369 (1980); 23 723 (1982); 33 5981 (1992); 34 1355 (1993)
JOC 44 3397 (1979); 47 3219 (1982)
Syn 446 (1979)
CL 961 (1982)
JACS 104 4962 (1982); 112 5601 (1990)
- H₂C=CHC(=CH₂)CH₂SiMe₃**, TiCl₄ *Tetr* 39 883 (1983)
- H₂C=CHCH(OSiR₃)SiR₃**, TiCl₄ (product after hydrolysis is R'COCH₂CH₂CHO) *JOC* 43 2551 (1978)
- R²CH=CR¹CH(SPh)SiMe₃**, AlCl₃ (SE₂') *CC* 377 (1981)
- RSiR'₃**, AlCl₃ or TiCl₄ (R = vinylic) *CC* 633 (1975)
JCS Perkin I 2485 (1980); 2527 (1981)
TL 22 2985 (1981); 23 263 (1982); 27 4869 (1986)
JOC 46 2400 (1981) (intramolecular); 54 868 (1989); 56 6245 (1991); 59 3335 (1994)
SL 221, 499 (1992); 817 (1995)
- R'C≡CCH₂SiMe₃**, AlCl₃ (R = CR'=C=CH₂) *TL* 22 3401 (1981)
- RSiR'₃**; AlCl₃, ZnCl₂ or TiCl₄ (R = alkynyl) *Ber* 96 3280 (1963)
JOMC 37 45 (1972)
Syn 438 (1979); 29 (1981)
Helv 62 852 (1979); 64 1123 (1981); 65 13, 2413 (1982)
CC 459 (1981)
JOC 47 3219 (1982); 52 3662 (1987); 57 3203 (1992)
TL 23 3203 (1982); 28 5543 (1987); 33 1451 (1992)
Can J Chem 60 379 (1982)
JACS 106 3548 (1984); 107 6046 (1985)
- R₂NC≡CSiR'₃** *Ann* 1907 (1981)

R_4Sn , Pd catalyst ($R = 1^\circ$ alkyl, aryl, vinylic)	CL 1423 (1977) JOC 51 2405 (1986)
R_3SnR' , Pd catalyst ($R = 1^\circ$ alkyl, allylic, alkynyl, benzylic, aryl, vinylic)	CL 1423 (1977) JACS 100 3636 (1978); 105 6129 (1983); 112 9645 (1990); 113 9585 (1991); 116 8126 (1994); 117 634, 3306 (1995) JOC 44 1613 (1979); 47 2549 (1982); 48 4634 (1983); 53 3218, 6138 (1988); 54 4721 (1989); 57 1047, 5047 (1992); 58 3543, 6072 (1993); 59 332, 451, 2638, 4143, 7917 (1994); 60 6006 (1995) TL 24 4283 (1983); 27 2801 (1986); 28 759 (1987); 30 2393, 4249 (1989); 31 1857 (1990); 32 4341 (1991); 34 5445 (1993); 35 1027, 5177, 7435, 8955 (1994); 36 389, 2037, 2469 (1995) SL 875 (1992); 123 (1994) (on polymer) Org Syn Coll Vol 8 268 (1993)
$R_2NCH_2Sn(n-Bu)_3$	TL 27 2361 (1986)
$RCH(OR)Sn(n-Bu)_3$, cat $PdCl_2(PPh_3)_2$, cat CuCN	TL 34 8007 (1993)
$RCHXS(n-Bu)_3$ ($X = OR, O_2CR, NR_2$), cat $PdCl_2(PPh_3)_2$, cat CuCN	JACS 116 1 (1994)
 $Sn(n-Bu)_3$, cat $Pd(PPh_3)_4$	TL 31 2637 (1990)
$(H_2C=CHCH_2)_4Sn$, CsF	JACS 110 7737 (1988)
$RCH=CHCH_2SnR'_nCl_{3-n}$ ($n = 1-3$; $R' = n-Bu$ or $RCH=CHCH_2$)	JOMC 258 291 (1983)
R_3SnR' , cat $ClRh(PPh_3)_3$ ($R =$ allylic, benzylic)	JOMC 129 C36 (1977) JOC 53 542 (1988)
R_3SnR' , $AlCl_3$ ($R =$ vinylic)	BSCF 1251 (1977)
$E-(n-Bu)_3SnCH=CHSn(n-Bu)_3$, $AlCl_3$ (monoacylation)	TL 27 5947 (1986) JOC 52 1493 (1987)
R_3SnR' ($R =$ alkynyl), Δ	Ann 716 29 (1968)
$ROC\equiv CSnR'$	TL 22 2637 (1981) Org Prep Proc Int 14 189 (1982)
$R_2NC\equiv CSnR'$	Angew Int 18 405 (1979) Ann 1907 (1981); 196 (1982)
$R''COSnR'_3$, cat $PdCl_2(PPh_3)_2$ ($R = R''CO$)	TL 26 6075 (1985)
R_4Pb , cat $Pd(PPh_3)_4$ ($R = 1^\circ$ alkyl)	CC 1302 (1987)
R_3PbR' ($R =$ alkynyl)	TL 2265 (1967) JCS C 317 (1968)
R'_4SbR ($R = Me, 1^\circ$ alkyl, aryl, benzylic, allylic)	JOC 57 774 (1992)
$n-Bu_4SbR$ ($R =$ benzylic, allylic)	JOC 57 774 (1992)

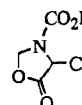

RM

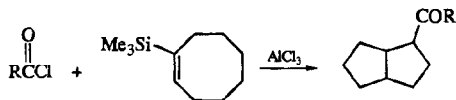
Cp_2ZrClR , AlCl_3 ($\text{R} = 1^\circ, 2^\circ$ alkyl; vinyl)	JACS 96 8115 (1974); 99 638 (1977)
Cp_2ZrClR , cat $\text{CuBr}\cdot\text{SMe}_2$ ($\text{R} = 1^\circ, 2^\circ$ alkyl; vinylic)	SL 718 (1992)
RMnX ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl; alkynyl; aryl; vinylic)	TL 3155 (1976); 22 1239 (1981); 26 1285 (1985); 27 4869 (1986); 29 3659 (1988); 30 3545, 7369 (1989); 33 5245 (1992); 36 6449 (1995) Syn 130 (1977); 37 (1984); 50 (1985) Can J Chem 58 287 (1980) Tetr 40 683 (1984)
RMnCl , cat CuCl ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl; aryl; vinylic)	TL 30 7369 (1989); 33 5245 (1992)
R_2Fe	TL 31 507 (1990)
Me_3FeLi	TL 31 507 (1990)
$\text{Fe}(\text{CO})_4^{2-}$, $\text{R}'\text{CH}-\text{CH}_2$ ($\text{R} = \text{R}'\text{CH}=\text{CH}$)	CL 1067 (1979)
$\text{RRh}(\text{CO})\text{L}_2$ ($\text{R} = 1^\circ$ alkyl, aryl, allylic)	JACS 97 5448 (1975) JOC 42 1194 (1977)
Li , naphthalene / $\text{CuCN}\cdot n\text{LiX}$ ($n = 1, 2$; $\text{X} = \text{Cl}, \text{Br}$) / RX ($\text{RX} = 1^\circ$ RBr, ArBr, allylic Cl or OAc)	JACS 113 4672 (1991); 114 5110 (1992) JOC 58 2483 (1993)
Li , naphthalene / CuI , PPh_3 / RX ($\text{RX} =$ 1° RBr or RCl, ArCl or ArI)	TL 29 4513 (1988) JOC 58 2483 (1993)
Li , naphthalene / $\text{CuI}\cdot\text{PEt}_3$ / ArX	JOC 53 4482 (1988) TL 34 2279 (1993)
Li , naphthalene / $\text{CuI}\cdot n\text{-Bu}_3\text{P}$ / ArX (Ar = polystyrene)	JOC 55 788 (1990)
Li , naphthalene / $\text{ThCu}(\text{CN})\text{Li}$ / RX ($\text{RX} = 1^\circ$ RBr, allylic chloride, ArBr or ArI)	JOC 58 2492 (1993)
$\text{Cu}\cdot\text{polymer}$ / RX ($\text{R} = 1^\circ$ alkyl, aryl)	JOC 55 788 (1990)
RCu	JOC 56 4744 (1991)
$\text{PhCH}_2\text{O}_2\text{CCH}(\text{NHBoc})\text{CH}_2\text{CH}_2\text{Cu}$	SL 219 (1993)
ArCu	JOC 56 4744 (1991); 60 2361 (1995)
$\text{RCu}\cdot\text{COD}$ ($\text{R} = 1^\circ$ alkyl)	CC 1030 (1982)
$\text{RCu}\cdot n\text{-Bu}_3\text{P}$ ($\text{R} = 1^\circ$ alkyl)	CC 1030 (1982)
RCu , LiI ($\text{R} = 1^\circ$ alkyl)	CC 1030 (1982)
$\text{ArCH}_2\text{Cu}\cdot\text{ZnI}_2$	JOC 58 2694 (1993)
$\text{R}_f\text{CF}=\text{CFCu}$	JACS 108 4229 (1986)

$\text{RC}\equiv\text{CCu}$, (LiI or Et_3N)	JOC USSR 3 1298 (1967) JACS 91 6464 (1969) TL 2659 (1970); 29 2279 (1988) JOC 40 131 (1975); 46 4107 (1981)
R_2CuLi ($\text{R} = 1^\circ$ alkyl, aryl)	BSCF 797 (1970) TL 4647 (1970); 2113 (1971) JACS 94 5106 (1972); 108 3731, 4603 (1986) CC 1030 (1982) JOC 52 4274 (1987)
	JOC 58 2920 (1993)
$(\text{Me}_3\text{Si})_2\text{CuLi}$	JOC 53 3612 (1988)
$(\text{Z-RCH}=\text{CH})_2\text{CuLi}$, [cat $\text{Pd}(\text{PPh}_3)_4$]	Tetr 42 1369 (1986)
$\text{R}_2\text{C}=\text{CHCu}\cdot\text{MgX}_2$, HMPA or cat $\text{Pd}(\text{PPh}_3)_4$	See page 452, Section 2.28.
R_2CuMgX ($\text{R} = 1^\circ, 3^\circ$ alkyl; allylic; aryl)	TL 2113 (1971); 3377 (1980) JOMC 188 293 (1980)
$(\text{RCuMe})\text{Li}$ ($\text{R} = 2^\circ, 3^\circ$ alkyl)	TL 21 3151 (1980)
$(\text{RCuMe})\text{MgX}$ ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl; aryl)	JOC 41 2750 (1976)
$[\text{RCuC}\equiv\text{CC}(\text{CH}_3)_3]\text{Li}$ ($\text{R} = 1^\circ$ alkyl)	CC 1030 (1982)
$\text{RCu}(\text{CN})\text{Li}$ ($\text{R} = 1^\circ$ alkyl)	CC 1030 (1982) JACS 116 11723 (1994)
$\text{Me}_3\text{SiCH}=\text{CHCH}_2\text{Cu}(\text{CN})\text{Li}$	TL 22 2985 (1981)
$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$ ($\text{R} = 1^\circ$ alkyl)	CC 1030 (1982)
$(\text{Me}_3\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$	JOC 53 3612 (1988)
$\text{RCu}(\text{CN})\text{ZnX}$	JOC 53 2390 (1988); 56 1445, 5974 (1991) TL 30 5069 (1989); 31 1833, 7575 (1990); 34 5261 (1993); 36 1023 (1995)
$\text{NCCH}_2\text{CH}_2\text{Cu}(\text{CN})\text{ZnI}$	TL 29 2395 (1988); 30 5069 (1989)
$\text{ArCH}_2\text{Cu}(\text{CN})\text{ZnX}$	JOC 53 5789 (1988)
$\text{RCO}_2\text{CH}_2\text{Cu}(\text{CN})\text{ZnI}$	JOC 54 5202 (1989); 58 588 (1993)
$\text{AcOCHRCu}(\text{CN})\text{ZnBr}$	JOC 55 4791 (1990); 58 588 (1993)
$\text{RO}_2\text{CCH}(\text{NHBoc})\text{CH}_2\text{Cu}(\text{CN})\text{ZnI}$	JOC 60 2210 (1995)
	SL 819 (1995)
$\text{ArCu}(\text{CN})\text{ZnX}$	TL 31 4413 (1990); 35 1047 (1994) JOC 56 1445 (1991) JACS 114 3983 (1992)

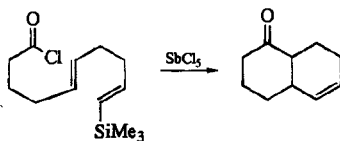
RM

$\text{RCH}=\text{CHCu}(\text{CN})\text{ZnX}$	JOC 56 1445 (1991)
$(\text{R}'\text{SO}_2\text{CH}_2\text{CuR})\text{Li}$ ($\text{R}' = \text{Me, Ph; R} = 1^\circ, 2^\circ, 3^\circ$ alkyl, aryl)	CC 358, 1030 (1982)
$(\text{CH}_3\text{SOCH}_2\text{CuR})\text{Li}$ ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl; aryl)	JOC 52 1885 (1987)
$[\text{CH}_3\text{SOCH}_2\text{Cu}(\text{CN})\text{R}]\text{Li}_2$ ($\text{R} = 2^\circ$ alkyl)	JOC 52 1885 (1987)
$(\text{PhSCuR})\text{Li}$ ($\text{R} = 2^\circ, 3^\circ$ alkyl)	JACS 95 7788 (1973) Syn 662 (1974) Org Syn 55 122 (1976) CC 1030 (1982) Org Syn Coll Vol 6 248 (1988) JOC 59 3142 (1994)
$(t\text{-BuOCuR})\text{Li}$ ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl)	TL 1815 (1973); 24 3165 (1983) JACS 95 7788 (1973)
$(\text{RCuNR}'_2)\text{Li}$ ($\text{R}' = \text{Et, Ph; R} = 1^\circ$ alkyl)	CC 1030 (1982)
$(\text{RCuNCy}_2)\text{Li}$ ($\text{R} = 1^\circ, 3^\circ$ alkyl)	JACS 104 5824 (1982) CC 1030 (1982)
$(\text{RCuPPh}_2)\text{Li}$ ($\text{R} = 1^\circ, 3^\circ$ alkyl)	JACS 104 5824 (1982) CC 1030 (1982)
$(\text{RCuPCy}_2)\text{Li}$ ($\text{R} = 1^\circ$ alkyl)	CC 1030 (1982)
$\text{RC}\equiv\text{CAg}$	JACS 78 1675 (1956) TL 1303 (1970)
RI, Zn-Cu ($\text{R} = 1^\circ$ alkyl)	Ber 80 129 (1947)
$\text{RI, Zn-Cu / cat Pd(PPh}_3)_4$ ($\text{R} = 1^\circ, 2^\circ$ alkyl)	TL 26 5529, 5559 (1985)
$\text{RI, Zn-Cu / cat PdCl}_2(\text{PPh}_3)_2$ ($\text{R} = \text{CHRCHRCO}_2\text{R}$)	TL 34 5939 (1993)
$\text{ArCH}_2\text{Br, Zn, PdCl}_2(\text{PPh}_3)_2$	CL 1135 (1981) TL 26 4777 (1985)
RZnX ($\text{R} = 2^\circ, 3^\circ$ alkyl)	TL 35 7205 (1994)
RZnX or R_2Zn ($\text{R} = 1^\circ, 2^\circ$ alkyl; aryl)	JACS 69 2350 (1947); 71 3804 (1949) Org Rxs 8 28 (1954)
ArCH_2ZnBr ($\text{R}' = \text{CCl}_3$)	TL 33 3435 (1992)
$\text{RZnX, cat PdCl}_2(\text{PPh}_3)_2-i\text{-Bu}_2\text{AlH}$ ($\text{R} = 2^\circ$ alkyl)	TL 32 1573 (1991)
$\text{RZnX, cat Pd(PPh}_3)_4$ ($\text{R} = 1^\circ, 3^\circ$ alkyl; benzyl; aryl; vinylic; alkynyl)	TL 24 5181 (1983); 28 1055 (1987) JOC 58 2637 (1993) JACS 116 11723 (1994)
$\text{EtO}_2\text{CCH}_2\text{ZnBr, cat Pd(0)}$	CL 1559 (1982)
$\text{EtO}_2\text{C(CH}_2)_3\text{ZnI, cat Pd(PPh}_3)_4$	Org Syn 67 98 (1989) Org Syn Coll Vol 8 274 (1993) SL 38 (1995)

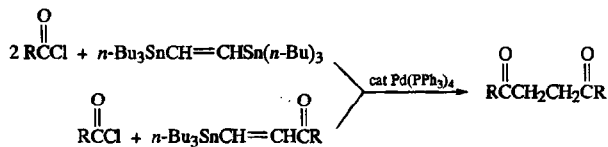
	SL 819 (1995)
$\text{BnO}_2\text{CCH}(\text{NHBoc})\text{CH}_2\text{ZnI}$, Pd catalyst	CC 644 (1989) SL 735 (1990) JOC 57 3397 (1992) TL 34 2985 (1993); 35 4417 (1994)
$(\text{EtO}_2\text{CCH}_2\text{CH}_2)_2\text{Zn}$, Me_3SiCl , HMPA	JOC 50 2802 (1985)
$(\text{EtO}_2\text{CCH}_2\text{CH}_2)_2\text{Zn}$, Me_3SiCl , CuI	JACS 106 3368 (1984)
$(\text{RO}_2\text{CCH}_2\text{CH}_2)_2\text{Zn}$, cat $\text{PdCl}_2(o\text{-Tol}_3\text{P})_2$	TL 27 83 (1986); 28 337 (1987)
$(\text{RO}_2\text{CCH}_2\text{CH}_2)_2\text{Zn}$; HMPA or cat $\text{PdCl}_2(\text{PPh}_3)_2$ or cat $\text{CuBr}\cdot\text{SMe}_2$	JACS 109 8056 (1987)
R_2Zn , $\text{CuCN}\cdot 2\text{LiCl}$ ($\text{R} = 1^\circ, 2^\circ$ alkyl)	JOC 57 1956 (1992); 60 3311 (1995) SL 410 (1994)
	TL 30 6039 (1989) JOC 58 2958 (1993)
ArZnX , cat $\text{Pd}(\text{PPh}_3)_4$	JOC 60 2298 (1995)
ArMe_2ZnLi , cat $\text{Pd}(\text{PPh}_3)_4$	JOC 59 4717 (1994)
$\text{R}_2\text{C}=\text{CHRZnX}$, cat Pd	SL 886 (1992) JOC 58 4897 (1993); 60 290 (1995)
$\text{F}_2\text{C}=\text{CRZnX}$, cat CuBr ($\text{R} = \text{F}, \text{CF}_3$)	BCSF 876 (1986) TL 32 4271 (1991)
$\text{RC}\equiv\text{CZnX}$	JOC USSR 2 1859 (1966)
$\text{RC}\equiv\text{CZnCl}$, cat $\text{Pd}(\text{PPh}_3)_4$	JACS 112 5601 (1990) JOC 60 3550 (1995)
RCdX or R_2Cd , MgX_2 or LiX ($\text{R} = 1^\circ > 2^\circ > 3^\circ$ alkyl; aryl)	JACS 67 740 (1945); 72 5333 (1950) Chem Rev 40 15 (1947) (review) Org Rxs 8 28 (1954) (review) Org Syn Coll Vol 3 601 (1955) JCS A 453, 456 (1966) Can J Chem 58 287 (1980) JOC 47 2590 (1982)
RCdX or R_2Cd , FeCl_3 ($\text{R} = 1^\circ$ alkyl)	JOC 26 1772 (1961)
$\text{RC}\equiv\text{CCdX}$	JOC USSR 3 210 (1967); 4 2032 (1968)
R_2Hg , cat $\text{Pd}(\text{PPh}_3)_4$ ($\text{R} = 1^\circ$ alkyl, aryl)	CL 951 (1975)
ArHgCl , cat $\text{Pd}(\text{PPh}_3)_4$	JOC 54 4141 (1989)
$\text{RCH}=\text{CHCH}_2\text{HgCl}$, AlCl_3 (SE_2')	TL 29 6761 (1988) JOC 58 2846 (1993)
$\text{RCH}=\text{CHHgCl}$, AlCl_3	JOC 43 710 (1978)
$\text{RCH}=\text{CHCH}_2\text{SmCp}_2$	TL 32 629 (1991)



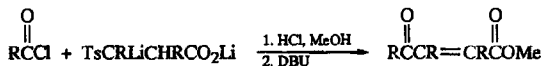
TL 30 7461 (1989)



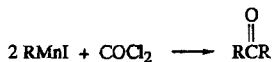
TL 26 1131 (1985)



JOC 59 4179 (1994)

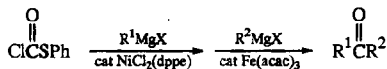


JOC 59 3202 (1994)



R = 1° alkyl

BSCF 570 (1977)



See page 1383, Section 2.1.

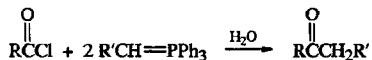


ArLi

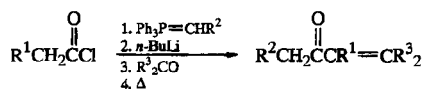
TL 30 989 (1989)

RMgX (R = 1°, 2° alkyl; aryl), CuBr, LiBr

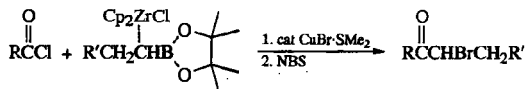
TL 36 7305 (1995)



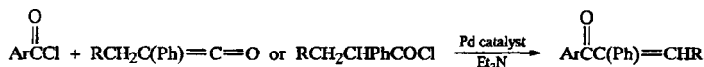
Ber 95 1513 (1962)



TL 31 2591 (1990)

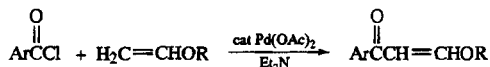


TL 36 5665 (1995)

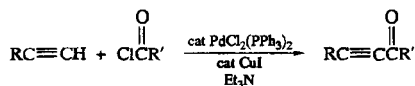


TL 26 5143 (1985)

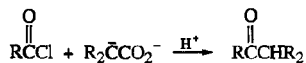
JOC 52 3186 (1987)



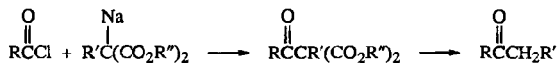
JOC 53 4257 (1988)



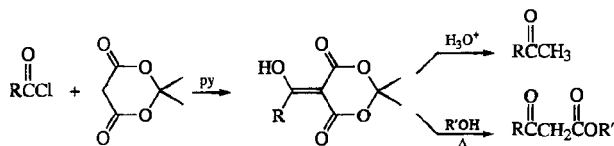
Syn 777 (1977)



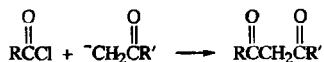
See page 1386, Section 2.5.



See page 1528, Section 22.



See page 1528, Section 22.

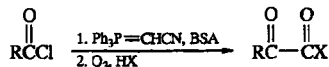


Org Rxs 8 59 (1954) (review)

JACS 107 1280 (1985)

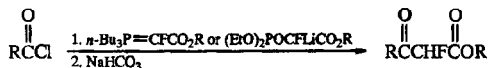
JOC 54 1485, 1785 (Me_2Zn , HMPA) (1989)

TL 34 8305 (1993)

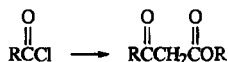


X = OH, OR, NHR

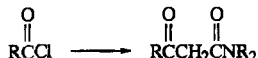
JOC 59 4364 (1994)



TL 30 6113 (1989)



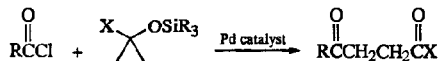
See page 1528, Section 22, for this and related reactions.



See page 1528, Section 22, for this and related reactions.



See page 1528, Section 22, for this and related reactions.

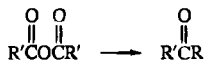


X = R, OR

TL 30 6541 (1989)

JOC 56 2809 (1991)

2.7. From Acid Anhydrides



RX (R = allylic, benzylic), electrolysis

TL 27 4175 (1986)

 ArSOCH_2Li

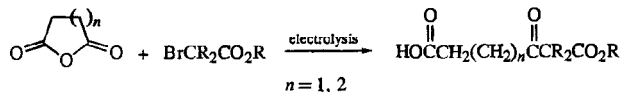
JOC 56 2317 (1991)

SL 167 (1992)

 $\text{R}_2\text{C}(\text{Li})\text{SO}_2\text{Ph}$

TL 32 4457 (1991)

ArLi	JOC 41 1268 (1976); 55 4971 (1990); 59 8220 (1994) TL 34 8063 (1993)
ArLi, TMEDA	Ann 2247 (1981)
RC≡CLi	Ber 97 1649 (1964) Monatsh 102 214 (1971)
RMgX (R = 1°, 2°, 3° alkyl; aryl)	JCS 1367, 1370 (1935) JACS 64 2226 (1942); 67 154 (1945); 80 1225 (1958) JOC 13 592 (1948); 25 214 (1960); 51 3502 (1986); 57 5532, 7285 (1992) CL 663, 687 (1974) Austral J Chem 30 427 (1977) TL 27 2001 (1986); 33 4675 (1992); 34 8063 (1993); 36 6413 (1995)
RMgX, HMPA, (5% FeCl ₃) (R = 1°, 2° alkyl)	Compt Rend C 275 511 (1972)
ArMgX, TMEDA	Angew 90 1000 (1978) JOC 46 2601 (1981) Ann 2247 (1981)
RC≡CMgX	JACS 58 1861 (1936)
EtAlCl ₂	JACS 110 2242 (1988)
Me ₃ Al	JACS 113 4607 (1991)
LiAlR ₄ , cat CuX or CuCl ₂ (R = 1° alkyl)	CL 623 (1979)
ArSiMe ₃ , cat KO- <i>t</i> -Bu	Angew Int 20 265 (1981)
RC≡CSiMe ₃ , AlCl ₃	TL 28 5543 (1987)
ArSn(<i>n</i> -Bu) ₃ , cat PdCl ₂ (PPh ₃) ₂ (R' = CF ₃)	SL 165 (1995)
RSnR' ₃ , AlCl ₃ (R = vinylic)	BSCF 1251 (1977)
RMnX (R = 1° alkyl, aryl, alkynyl, vinylic)	Syn Commun 9 639 (1979) Tetr 40 683 (1984) Syn 37 (1984); 50 (1985)
ArLi, CuBr·SMe ₂ (R' = CF ₃)	TL 32 2003 (1991)
RC≡CLi, CuI	JACS 109 6899 (1987)
R ₂ CuLi	JOC 58 3188 (1993)
Ar ₂ CuMgX	JOMC 188 293 (1980)
R ₂ Cd (R = 1° alkyl, aryl > 2°, 3° alkyl)	JOC 6 462 (1941)
R ₂ C(CeCl ₂)SO ₂ Ph	TL 32 4457 (1991)



JOC 57 4013 (1992)

XReagent

OR

RCHLiCOR

See page 1476, Section 2.

RCHLiCO₂R

See page 1724, Section 2.

RCHLiCO₂SiMe₃ (decarboxylation also)

TL 3713 (1978)

RCHLiCONR₂

Tetr 37 307 (1981)

RCHLiCN

See page 1778, Section 4.

-CR(CO₂Et)₂

See page 1801, Section 6.

R'MgX

JOC 22 245 (1957)

RMnI

CL 687 (1974)

Et₂Cd

Syn 50 (1985)

i-Bu

R'MgX

JOC 22 245 (1957)

Ar

R'MgX

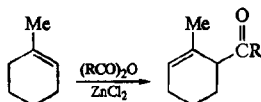
CL 663, 687 (1974)

JOC 58 4191 (1993)

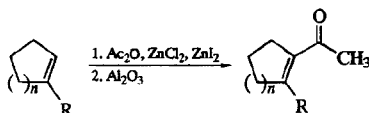


Syn Commun 8 59 (1978)

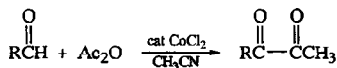
CC 412 (1986)



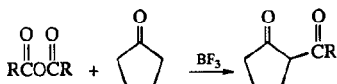
JACS 102 3848 (1980); 112 8126 (1990)

 $n = 1, 2$; R = H, Me

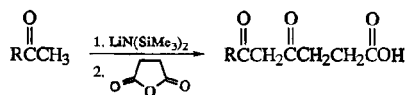
TL 22 3351 (1981)



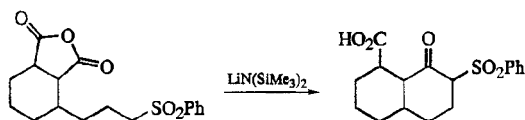
JOC 58 5518 (1993)



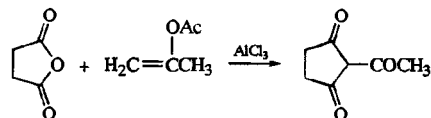
See page 1476, Section 2.



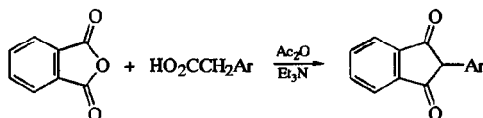
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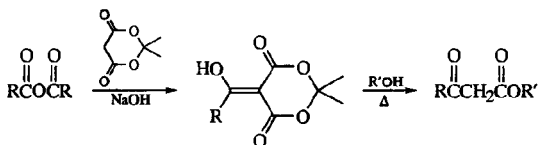
JACS 106 3811 (1984)



Org Syn Coll Vol 6 28 (1988)

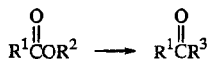


JOC 54 1485 (1989)



See page 1528, Section 22, for this and related reactions.

2.8. From Esters and Lactones

R³CH₃Reagents-CH₂SOCH₃ / Al(Hg), H₂O

JACS 87 1345 (1965)

JOC 31 2355 (1966); 46 4825
(1981); 59 1184 (1994)-CH₂SOCH₃ / Zn, NaOH

JOC 52 4477 (1987)

LiCH₂SOAr / Raney Ni

SL 449 (1992)

-CH₂SO₂CH₃ / Al(Hg), H₂O

JOC 33 61 (1968)

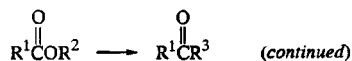
Li₂CHSO₂Ph / Al(Hg) or


JOC 54 3755 (1989)

Na(Hg)

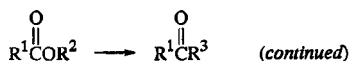
-CH₂SONaAr / H₂O

JACS 90 5548 (1968)

R³Reagents

	$R_3\text{SnCH}_2\text{Li}$ ($R = \text{Me, Ph}$)/ H_2O	TL 27 4339 (1986) JOC 53 1207 (1995)
	$\text{LiCH}_3\text{Mg}[\text{N}(\text{SiMe}_3)_2]_2$	JOC 58 3731 (1993)
	CH_3MgBr , $-78^\circ\text{C}/\text{H}_2\text{O}$ ($R^2 = 2\text{-pyridyl}$)	TL 28 1603 (1987)
CH_2R	$\text{ArSOCHLiR}/\text{Raney Ni}$	JOC 57 7235 (1992)
	$\text{ArSO}_2\text{CHLiR}/\text{Na(Hg)}$	SL 167 (1992)
	$\text{PhSO}_2\text{CRLi}_2/\text{Na(Hg)}$ or $\text{Al(Hg)}, \text{H}_2\text{O}$	JOC 45 4002 (1980); 47 564 (1982); 56 2317 (1991)
	RCH_2MgX	JOC 58 2718 (1993)
	$\text{R}\bar{\text{C}}\text{H}[\text{B(OR)}_2]_2$	SL 199 (1993)
	$\text{RCH[B(OR)}_2]_2$	JACS 99 3196 (1977)
	$\text{Ph}_3\text{P}=\text{CHR}/\text{H}_2\text{O}$ ($R^1 = R_f$)	Organomet 1 20 (1982) JOC 57 3807 (1992)
$\text{CH}_2\text{CH}_2\text{R}$	 (from $\text{RC}\equiv\text{CH}$, $\text{9-BBN, MeLi}/\text{H}_2\text{O}$ ($R^1 = \text{Ph}$))	CL 1193 (1981)
1° alkyl	RLi	JACS 109 8071 (1987) ($R^1 = \text{RCF}_2$)
	AlCl_2 ($R^2 = 8\text{-quinoliny}$)	J Gen Chem USSR 51 1434 (1981); 52 1170 (1982)
	R_3Al , AlCl_3 ($R^2 = 8\text{-quinoliny}$)	J Gen Chem 52 1170 (1982)
	1° RI, cat NiCl_2 , $\text{Zn}/\text{H}_3\text{O}^+$	CL 531 (1981)
$1^\circ, 2^\circ$ alkyl	RMgX , HMPA	Compt Rend C 273 1543 (1971)
1° alkyl, aryl	RMgX , Et_3N	Syn 877 (1980) JOC 59 3575 (1994)
$1^\circ, 2^\circ$ alkyl; 1° benzylic; aryl	$\text{RMgX}/\text{H}_2\text{O}$ ($R^1 = \text{CF}_3$)	JOC 52 5026 (1987)
Ph	PhMgCl , $\text{Me(MeO)NH}\cdot\text{HCl}$	TL 36 5461 (1995)
Ar	ArLi ($R^1 = \text{CF}_3$)	JOC 52 5026 (1987); 56 893 (1991) JACS 115 9939 (1993)
allylic	$\text{RCH}=\text{CRCH}_2\text{MgCl}/\text{KH}$	TL 23 335 (1982)
	$\text{R}_3\text{Al}_2\text{Cl}_3$ ($R^2 = 8\text{-quinoliny}$)	J Gen Chem USSR 51 1434 (1981)
$\text{CH}_2\text{CHR}'\text{CH}=\text{CR}_2$	$\text{Ph}_3\text{P}=\text{CHCH}=\text{CH}_2/\text{R}'\text{Li}/\text{R}_2\text{CO}$	TL 31 3161 (1990) ($R^1 = \text{CF}_3$)
$\text{CHMeCH}_2\text{CMc}=\text{CH}_2$	$\text{H}_2\text{C}=\text{C(Me)MgBr}$	Austral J Chem 30 427 (1977)
CH_2Cl	ICH_2Cl , MeLi	JOC 60 6696 (1995)

CHXR (X = Cl, Br)	LiCHXR	Syn 68 (1981) TL 25 835 (1984)
CHClBr	LiCHClBr	TL 33 4041 (1992)
CHBr ₂	LiCHBr ₂	JOC 53 1227 (1988); 57 7194 (1992)
CF ₃	CF ₃ SiMe ₃ , cat <i>n</i> -Bu ₄ NF CF ₃ ZnBr	TL 30 5243 (1989) TL 29 1029 (1988)
CF ₂ CF ₃	LiCF ₂ CF ₃	JOC 52 2481 (1987)
CH ₂ OH	Me ₃ SiCHLiOCO ₂ Li / H ₃ O ⁺	TL 28 1847 (1987)
CH(OH)R	RCHLiOCO ₂ Li / H ₃ O ⁺	TL 28 1847 (1987) (R = SiMe ₃) Syn 415 (1987) (R = Ph)
CH(NH ₂)Ph	PhCHLiLiLiCO ₂ Li / H ₃ O ⁺	Syn 415 (1987)
CH ₂ SPh	LiCH(SPh)SiMe ₃	TL 22 2803 (1981)
CHRSPh	R ⁻ C(SPh)[B(OR) ₂] ₂	Organomet 1 280 (1982)
CH(SMe) ₂	LiC(SMe) ₃	JOC 60 6017 (1995)
CH(SPh) ₂	LiCH(SPh) ₂	TL 35 7327 (1994)
C(SMe) ₃	LiC(SMe) ₃	JOC 60 6017 (1995)
CHRSOAr	LiCHRSOAr	JOC 58 7235 (1992); 59 533 (1994)
CH ₂ SO ₂ Ar	Li ₂ CHSO ₂ Ar	JOC 54 3755 (1989) SL 1015 (1994)
CHRSO ₂ Ar	RCH(Li)SO ₂ Ar	JOC 57 7235 (1992); 59 2014 (1994) (intramolecular); 60 5048 (1995) (5-alkanolide)
	RC(Li) ₂ SO ₂ Ar	JOC 45 4002 (1980); 47 564 (1982); 56 2317 (1991) TL 29 3609 (1988) (4- and 5-alkanolides) SL 771 (1990)
CH ₂ SO ₂ NR ₂	LiCH ₂ SO ₂ NR ₂	TL 31 3875 (1990)
CClRCH=CH ₂	RCCl=CHCH ₂ Li / H ₃ O ⁺	JOMC 215 1 (1981)
CCl=CHCH ₃	ClCH=CHCH ₂ Li / H ₃ O ⁺	JOMC 215 1 (1981)
C≡CR	LiC≡CR LiC≡CR, BF ₃ ·OEt ₂	Syn 307 (1978) Syn 421 (1986) JOC 53 6013 (1988) (R ¹ = CF ₃ , CHF ₂); 59 957 (1994) (R ¹ = CF ₃) TL 32 2219, 2223 (1991); 35 3521 (1994)
CH ₂ COR	⁻ CH ₂ COR	See page 1476, Section 2.

R³ReagentsCH₂CO₂RLiCH₂CO₂R

See page 1724, Section 2.

CHRCN

⁻CHRCN

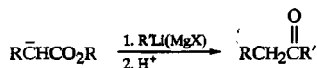
See page 1801, Section 6.

RCH₂CN, cat SmCl₃,
electrolysis

SL 293 (1992)

SnR₃R₃SnLi, BF₃·OEt₂

JOC 54 2966 (1989)

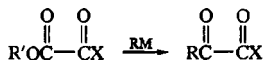


JOC 53 1828 (1988)

JACS 110 6909 (1988) (chiral protonation)



Helv 69 228 (1986)

XRM

OR

ArLi

JOC 52 5026 (1987)

RMgX (R = 1°, 3° alkyl)

Syn Commun 11 943 (1981)

JOC 52 5026 (1987)

TL 29 423 (1988)

ArMgX

JOC 45 2883 (1980); 52 5026
(1987)

Syn Commun 11 943 (1981)

TL 29 1029 (1988)

CF₃ZnBr

TL 31 3433 (1990)

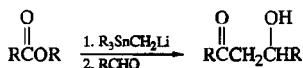
NR₂

RMgX (R = 2°, 3° alkyl)

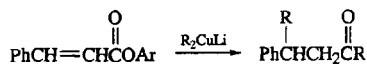
JACS 115 9925 (1993)



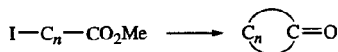
Org Syn Coll Vol 1 238 (1941)



JOC 53 1207 (1988)



TL 32 7277 (1991)

Reagent*n*

RLi, -100 °C

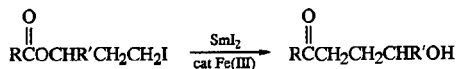
4, 5

TL 26 4987 (1985); 27 519 (1986); 31 4027 (1990); 32 6885 (1991)

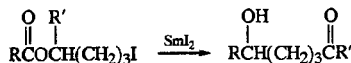
SmI₂

3-6

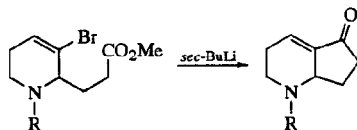
JOC 58 7216 (1993)



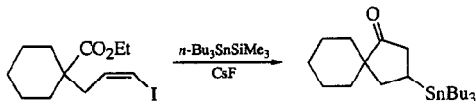
JOC 59 3445 (1994)



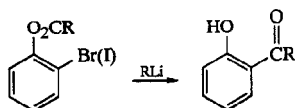
JACS 115 5821 (1993)



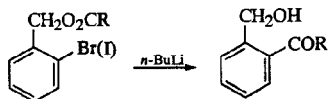
JACS 109 6115 (1987)



JOC 58 2972 (1993)

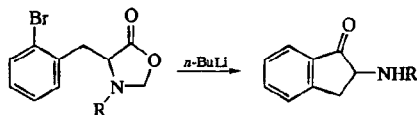


See page 1310, Section 9.18.

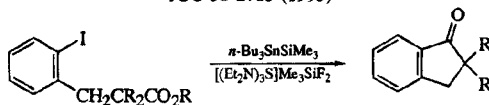


CC 166 (1992)

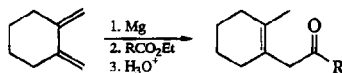
JOC 59 5147 (1994)



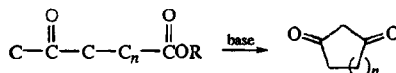
JOC 58 2763 (1993)



JOC 58 2972 (1993)



JACS 114 4415 (1992); 117 5429 (1995)

 \underline{n}

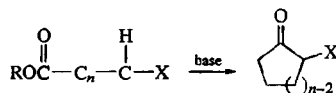
1

BSCF 645 (1965)

Org Syn Coll Vol 6 774 (1988)

2

JOC 57 3846 (1992)

 \underline{X}

CN

 \underline{n}

3-5

JACS 105 7713 (1983)

TL 28 4641, 4645 (1987); 29 147 (1988)

SOPh

5

TL 31 3783 (1990); 32 275 (1991)

SO₂R

3-6, 8

JACS 77 5063 (1955)

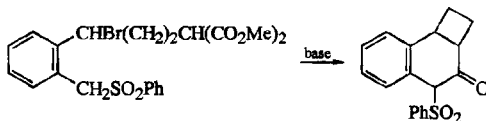
TL 29 5169 (1988); 31 5179 (1990); 34 7017 (1993); 35

5369, 6847 (1994); 36 5331 (1995)

Bull Korean Chem Soc 12 461 (1991)

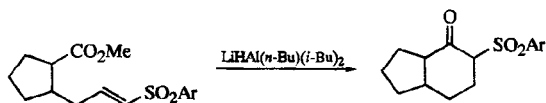
JOC 60 6000 (1995)

SL 779 (1995)



TL 28 709 (1987)

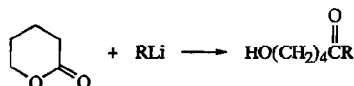
JOC 53 1912 (1988)



TL 34 8553 (1993)

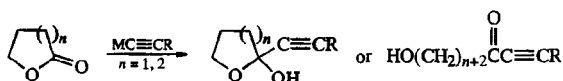


JOC 54 3514 (1989)



JOC 47 3140 (1982); 54 2044 (1989); 58 291 (1993)

TL 28 651 (1987); 34 1851 (1993)

 $\text{MC}\equiv\text{CR}$ $\text{LiC}\equiv\text{CR}$

Syn Commun 3 135 (1973); 6 503 (1976)

TL 937 (1978); 28 3651 (1987); 29 2819 (1988); 30 5993 (1989); 31 4279 (1990)

JOC 47 615, 3140 (1982); 53 652 (1988); 54 1157 (1989); 55 5894 (1990); 57 132 (1992)

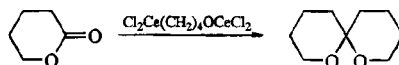
BCSJ 59 1521 (1986)

 $\text{LiC}\equiv\text{CR}, \text{BF}_3\cdot\text{OEt}_2$

JOC 48 4427 (1983)

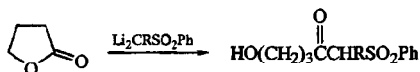
 $\text{HC}\equiv\text{CCeCl}_2$

JOC 58 4280 (1993)

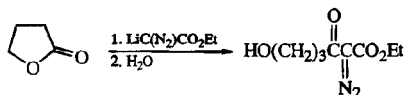


JACS 112 6389 (1990)

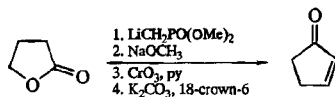
JOC 59 3142 (1994)



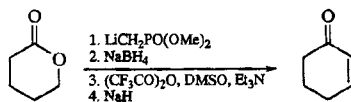
JOC 57 5596 (1992)



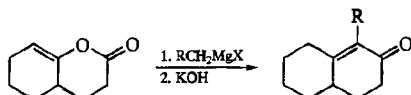
TL 28 5351 (1987)



JOC 53 5709 (1988)



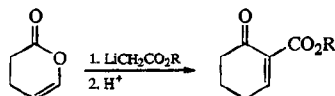
JOC 57 6693 (1992)



JACS 73 1856 (1951); 74 4223 (1952)

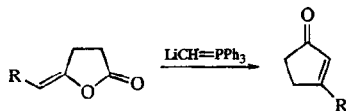
Syn 49 (1969) (review)

JOC 54 4702 (1989)

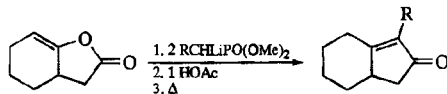


TL 31 3421 (1990)

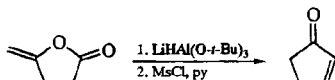
JOC 55 3004 (1990); 57 5979 (1992)



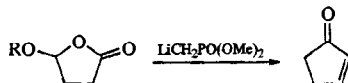
JOC 59 4450 (1994)



JACS 107 7967 (1985)



TL 29 5521 (1988)

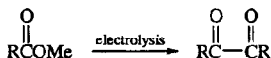


JOC 52 5457 (1987)

TL 31 1509 (1990)

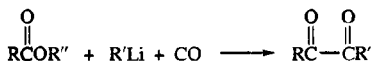


TL 35 5261 (1994)



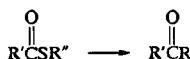
SL 901 (1991)

TL 36 4805 (1995)



JOC 56 5768 (1991); 58 5843 (1993)

2.9. From Thioesters



JACS 115 9842 (1993)

 R_3SnLi

JOC 54 2966 (1989)

 RMgX ($\text{R''} = 2\text{-pyridyl}$) ($\text{R} = 1^\circ, 2^\circ$ alkyl; aryl)

JACS 95 4763 (1973); 113 5337 (1991); 115 11393 (1993)

BCSJ 47 1777 (1974)

J Med Chem 23 1392 (1980)

JOC 46 3760 (1981); 51 938 (1986); 56 4823 (1991)

TL 23 2533 (1982)

SL 431 (1995)

 RMgX , cat $\text{Fe}(\text{acac})_3$ ($\text{R''} = \text{Ph}$; $\text{R} = 1^\circ, 2^\circ$ alkyl; aryl)

TL 26 3595 (1985)

 $\text{RC}\equiv\text{CSiMe}_3$, AgBF_4

TL 24 5131 (1983)

 R_2CuLi ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl; aryl)

JACS 96 3654 (1974); 108 4943 (1986)

CC 1231 (1981)

SL 937 (1993)

 $\text{RCu}(\text{CN})\text{Li}$ ($\text{R''} = 2\text{-benzothiazolyl}$)

SL 937 (1993)

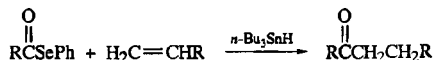
 $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$ ($\text{R''} = \text{Ph}$, 2-benzothiazolyl)

SL 937 (1993)

 $\text{ThCuR}(\text{CN})\text{Li}_2$ ($\text{R''} = \text{Ph}$)

SL 937 (1993)

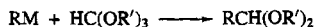
2.10. From Selenoesters



JOC 55 5442 (1990); 57 1429 (1992)

TL 31 227 (1990)

2.11. From Ortho Esters

RM

RMgX

TL 22 545 (1981)

RC≡CMgX

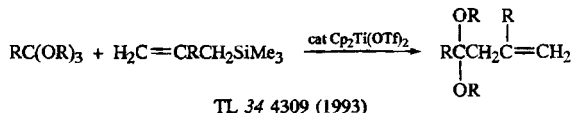
JCS 4244 (1955)

RCH=CR'CH₂MBr (M = Mg, Zn)

JOMC 222 1 (1981)

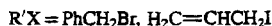
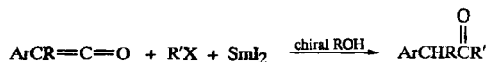
H₂C=CRCH₂SiMe₃, cat Cp₂Ti(OTf)₂

TL 34 4309 (1993)

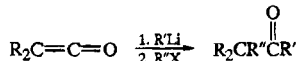


TL 34 4309 (1993)

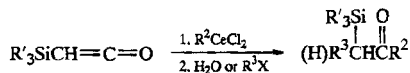
2.12. From Ketenes



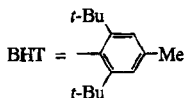
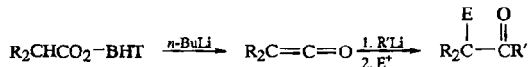
CL 551 (1992)



JOC 50 2105 (1985)



SL 401 (1991)

R'Ar, ArCH₂

Ar

E⁺

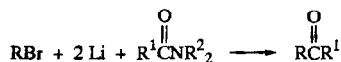
RCHO

ClCO₂R

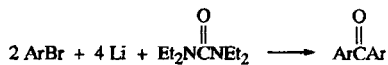
JACS 107 5396 (1985)

SL 827 (1992)

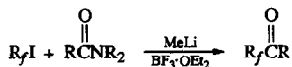
2.13. From Amides



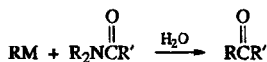
R = Et, Ph



Syn 160 (1973)



JOC 57 1504 (1992)

RM

RLi (R = 1°, 2° alkyl)

Ber 88 678 (1955)

JCS 4691 (1956)

JOC 24 701 (1959); 51 3290, 3566 (1986); 58 7507

(1993) (intramolecular)

Can J Chem 54 1098 (1976)

JOMC 177 5 (1979)

Angew Int 20 795 (1981)

TL 23 109 (1982); 25 811 (1984); 28 651, 3573 (1987)

SL 863 (1991) (intramolecular)

RC(CH₂)₃Li (R = H, Me)

TL 31 3763 (1990)

RCH(Li)OMOM

TL 33 3571 (1992); 36 6611 (1995)

JOC 50 4655 (1985)



TL 25 811 (1984)

ArLi

Ber 88 678 (1955)

Chem Ind 1596 (1957)

Bull Acad Sci USSR, Div Chem Sci 769 (1961)

Tetr 27 1221 (1971)

JOC 38 901 (1973); 57 2774 (1992) (intramolecular, fluorenone)

TL 25 811 (1984)

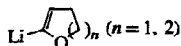
JACS 114 6227 (1992); 115 3458 (1993)

RCH=CHLi

TL 27 775 (1986) (intramolecular, 2-cyclopentenones and 2-cyclohexenones)

cycloalkenyl Li

JOC 55 4784 (1990)

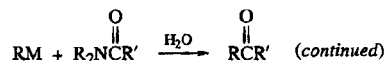


TL 35 7727 (1994)

RC≡CLi

TL 25 811 (1984)

CL 13 (1986)

RMRC≡CLi, BF₃·OEt₂

CL 35 (1983)
JOC 52 1372 (1987); 53 4282 (1988)
TL 34 4735 (1993)

RMgX (R = 1°, 2° alkyl)

JACS 61 232 (1939); 111 4392 (1989)
Ber 88 678 (1955)
Can J Chem 54 1098 (1976)
TL 25 811 (1984); 28 2999 (1987)
JCS Perkin I 795 (1985)
JOC 51 3566 (1986)

RMgX (R = vinylic)

JACS 111 4392 (1989)

ArMgX

Ber 88 678 (1955)
TL 25 811 (1984)
JOC 59 383 (1994); 60 1777 (1995)

RC≡CMgX

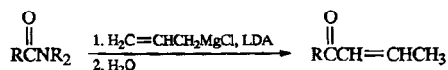
TL 25 811 (1984)

RCeCl₂ (R = 1° alkyl, vinylic)

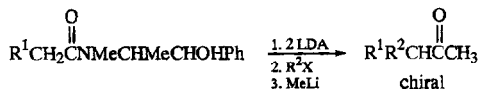
JACS 111 4392 (1989); 113 6672 (1991)

RLa(OTf)₂ (R = 1°, 2° alkyl; aryl)

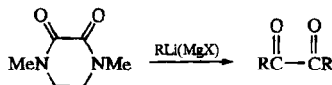
TL 28 4391 (1987)
JOC 55 3565 (1990)



Helv 69 228 (1986)

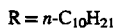
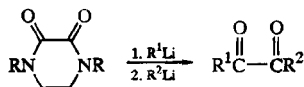


TL 3961 (1978)
JOMC 177 5 (1979)



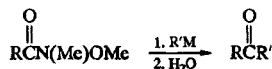
R = 1° alkyl, aryl

TL 34 571 (1993)
JOC 59 4988 (1994)
SL 975 (1994)
Tetr Asym 6 3 (1995)



JOC 59 4988 (1994)

SL 975 (1994)



Review: Org Prep Proc Int 25 15 (1993)

R'M $\text{CF}_3\text{CF}_2\text{Li}$

TL 33 3265 (1992)

 $\text{R}'\text{Li}$ ($\text{R}' = 1^\circ$ alkyl)

TL 22 3815 (1981); 27 5467 (1986); 32 2525 (1991)
 JACS 110 2506 (1988); 112 2998, 7001 (1990); 113 7613 (1991)
 JOC 58 5878 (1993)

 ArLi

TL 22 3815 (1981); 28 6331 (1987); 30 4783 (1989);
 32 2525 (1991); 34 2043 (1993)
 JOC 51 5106 (1986); 52 2615 (1987); 56 3750 (1991)
 JACS 113 5085 (1991); 115 3966 (1993)

 $\text{H}_2\text{C}=\text{CHCH}_2\text{Li}$

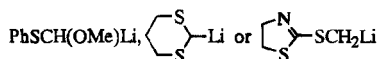
TL 32 2525 (1991)

 $\text{RCH}=\text{CR}'\text{Li}$

JACS 107 8066 (1985); 110 2506 (1988); 112 7001 (1990); 115 3360 (1993)
 JOC 57 1643, 5058, 5060 (1992)

 $\text{RC}\equiv\text{CLi}$

TL 22 3815 (1981); 28 1857 (1987); 32 1279 (1991);
 34 8003 (1993)
 JOC 50 2309, 3972 (1985); 57 2566 (1992); 59 5292 (1994); 60 3550 (1995)
 JACS 110 2301 (1988); 113 5384 (1991)



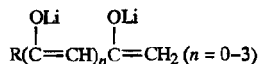
TL 28 1857 (1987)

 LiCH_2COR

See page 1476, Section 2.



See page 1516, Section 14.



See page 1528, Section 21.

 $\bar{\text{C}}\text{H}_2\text{CO}\bar{\text{C}}\text{HCO}_2\text{R}$

See page 1528, Section 22.

 $\text{LiCR}_2\text{CO}_2\text{R}$

See page 1724, Section 2.

LiCH₂CN

See page 1801, Section 6.

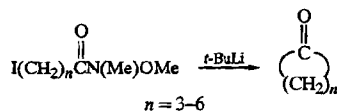
R'MgX (R' = 1° alkyl, allyl, benzyl, alkynyl, aryl, vinylic)

TL 22 3815 (1981); 28 1857, 6331 (1987); 32 1275 (1991)

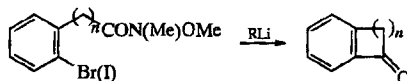
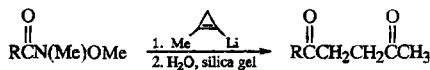
JOC 54 3913 (1989); 59 80 (1994); 60 1727, 6785 (1995)

JACS 112 3475 (1990); 113 7613 (1991); 115 9421 (1993)

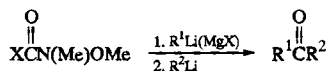
SL 700 (1995)



SL 151 (1990)

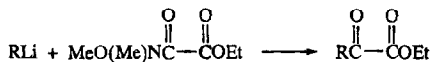
TL 32 721 (1991) ($n = 2$); 33 5431 (1992) ($n = 1$); 35 3771 (1994) ($n = 2$)

TL 31 2783 (1990)

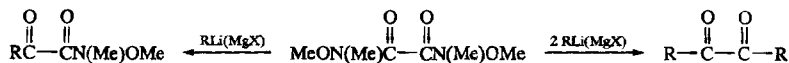
X = OEt, NMe₂, N(Me)OMe

TL 30 1773 (1989)

JOC 56 2911 (1991)

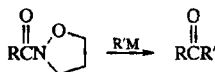
R = *n*-Bu, Ar, RC≡C

JOC 59 5763 (1994)



TL 33 1941 (1992)

JOC 60 5016 (1995)



$R'M$ RLi

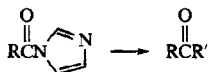
JOC 55 3511 (1990)

 $RC\equiv CLi$

JOC 51 5320 (1986)

 $RMgX$

JOC 55 3511 (1990)

 $LiCH_2SOCH_3$

JOC 54 5620 (1989)

 $LiCH_2SOAr$

TL 36 4559 (1995)

 $LiCH_2SO_2CH_3$

JOC 54 5620 (1989)

 $LiCHRCO_2R$

See page 1724, Section 2.

 $(Na)KCH_2NO_2$

Syn 478 (1978)

 $R'MgBr$ ($R' = \text{Me, Et, Ph}$)

Ann 655 90 (1962)

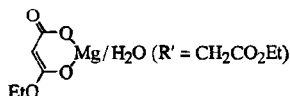
 $R'MgX$ ($R' = \text{aryl} > \text{alkyl}$; $R = CO_2R$)

JOC 46 211 (1981)

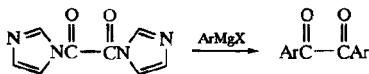
 $Mg(O_2CCHRCOXR)_2$ ($X = O, S$; $R' = CHRCOXR$)

Angew Int 18 72 (1979)

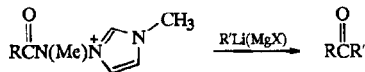
TL 28 5249 (1987)



BSCF 945 (1964)



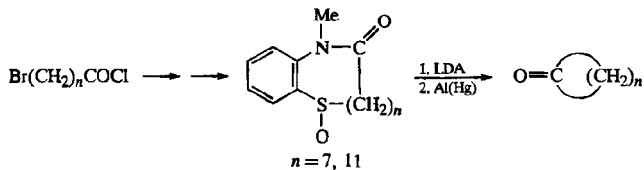
TL 34 3683 (1993)

 $R' = 1^\circ \text{ alkyl, aryl, alkynyl}$

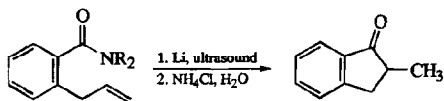
JOC 58 5862 (1993)



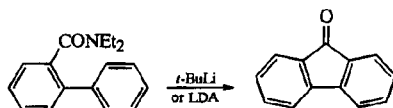
TL 28 1847 (1987)



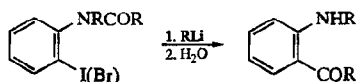
TL 4487 (1979)



TL 29 2183 (1988)

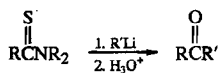


JOC 56 1683 (1991); 59 6508 (1994)



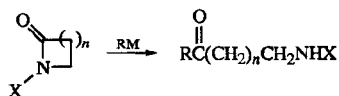
See page 1310, Section 9.18.

2.14. From Thioamides



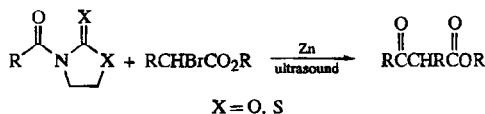
TL 28 1529 (1987)

2.15. From Imides

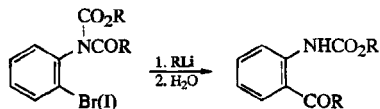


\underline{n}	\underline{X}	\underline{RM}	
1	COPh	MeMgX	Tetr 45 1283 (1989)
		RLi (R = alkyl)	JOC 59 5184 (1994)
		RCOCH ₂ Li	TL 36 4547 (1995)
		PhSO ₂ CHRLi	SL 51 (1993)
	Boc	RMgX (R = alkyl, aryl)	JOC 59 5184 (1994)
			TL 36 4543 (1995)
			JOC 59 5184 (1994)
2	CO ₂ CH ₂ Ph	R ₂ CuLi (R = alkyl)	SL 51 (1993)
		R ₂ Cu(CN)Li ₂ (R = alkyl)	SL 51 (1993)
		PhSO ₂ CHRLi	SL 51 (1993)
		MeLi	Tetr 45 1283 (1989)
	COR	RMgX (R = alkyl, aryl)	JOC 54 228 (1989)
			JOC 56 1822 (1991)
			TL 33 5589 (1992)

		RCOCH ₂ Li	TL 33 5589 (1992)
		RO ₂ CCH ₂ Li	See page 000, Section 000.
		RMgX (R = alkyl)	CL 2091 (1987)
			JOC 54 228 (1989); 56 1822 (1991)
		H ₂ C=CHCH ₂ MgX	TL 34 6317 (1993)
		H ₂ C=CHMgX	CL 2091 (1987)
			CL 2091 (1987)
		RC≡CMgX	TL 33 2553 (1992)
		ArMgX	CL 2091 (1987)
			JOC 54 228 (1989); 56 1822 (1991)
			TL 34 6317 (1993)
	CO ₂ CH ₂ Ph	RO ₂ CCH ₂ Li	See page 1724, Section 2.
		RMgX (R = alkyl)	JOC 54 228 (1989)
		ArMgX	JOC 54 228 (1989)
		H ₂ C=CHMgX	CL 2091 (1987)
3	COR	RMgX (R = alkyl)	JOC 54 228 (1989)
	Boc	PhSOCH ₂ Li	SL 139 (1993)
		RO ₂ CCH ₂ Li	See page 1724, Section 2.
		NCCH ₂ Li	See page 1801, Section 6.
		RMgX (R = alkyl)	JOC 54 228 (1989)
	CO ₂ CH ₂ Ph	ArMgX	JOC 54 228 (1989)
4	Boc	MeLi	SL 63 (1990)
		RMgX (R = alkyl)	JOC 54 228 (1989)
		ArMgX	SL 63 (1990)
5	Boc	RMgX (R = alkyl)	JOC 54 228 (1989)

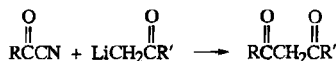


See page 1528, Section 22.

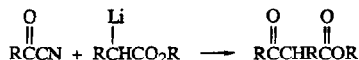


See page 1310, Section 9.18.

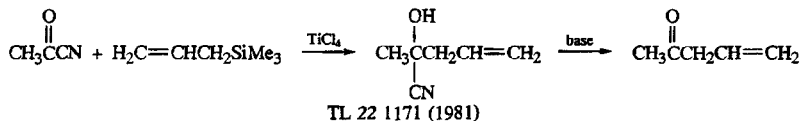
2.16. From Acid Nitriles



See page 1476, Section 2.



See page 1724, Section 2.

**2.17. From Nitriles**RLi (R = 1°, 2° alkyl; aryl) / H₃O⁺

Helv 729 (1962)
 JACS 92 336 (1970); 107 1028 (1985); 114 6603 (1992)
 TL 22 1509 (1981); 28 4329 (1987)
 JOC 47 4347 (1982); 53 4555 (1988)

RC(CH₂)₃Li (R = H, Me)

TL 31 3763 (1990)

Me₃SiCHLiOCO₂Li / H₃O⁺ (R = CH₂OH)

TL 28 1847 (1987)

R'CH=CHCH₂M (M = Li, MgX, ZnX) / H₃O⁺

JOMC 69 1 (1974) (review)

RMgX (R = 1° alkyl, aryl) / H₃O⁺

JACS 52 1267 (1930); 67 2059, 2197 (1945); 70 426 (1948); 72 876 (1950); 73 3948 (1951); 74 4607 (1952); 79 881 (1957); 109 3378 (1978); 110 900 (1988); 111 6311 (1989)
 BSCF 867 (1935)
 Bull Soc Chim Belg 44 523 (1935)
 JOC 15 359 (1950); 45 237 (1980); 54 2242 (1989); 57 3365, 3528 (1992); 58 5802 (1993); 59 3890 (1994)

Org Syn Coll Vol 3 26 (1955)
 JCS Perkin I 795 (1985)
 TL 29 4485 (1988); 32 6731 (1991)
 SL 921 (1993)

RMgX (R = 1° alkyl), Me₃SiCl / H₃O⁺

TL 32 6731 (1991)

RCH=CHMgX / H₃O⁺

TL 32 6731 (1991)

R₂C=CHCH₂MgX / H₃O⁺

Ann Chim 287 (1964)
 JACS 108 1311 (1986)

RMgX (R = 2°, 3° alkyl; aryl), cat CuBr / H₃O⁺

JOC 52 3901 (1987)

R₃P=CHR'' / H₃O⁺ (R = CH₂R'')

JACS 89 7009 (1967)

R''₂C=CHCH₂Br (R'' = H, Me), Zn(Ag) / H₃O⁺

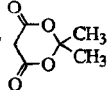
TL 22 649 (1981)

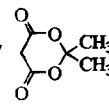
$R'CHBrCO_2R'$, Zn/H_3O^+ ($R = CHR'CO_2R'$) See page 1528, Section 22.

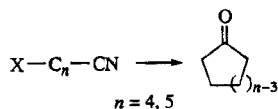
$R'CHBrCONR_2$, $Zn-Ag$, ultrasound/ H_3O^+ See page 1528, Section 22.
($R = CHR'CONR_2$, intramolecular)

$R'CH=CHCH_2TiCp_2/H_3O^+$ CC 342 (1981)
JOMC 224 327 (1982)

$ROCN \xrightarrow{S}$ (R = 2° alkyl), Ph_3SnH , cat AIBN/ H_3O^+ JOC 49 1313 (1984) (intramolecular)

HCl, MeOH/
, Et_3N , Δ /HCl ($R = Me$) Syn 130 (1981)

HCl, MeOH/
, Et_3N , Δ /NaOEt/
 H_3O^+ ($R = CH_2CO_2Et$) Syn 130 (1981)

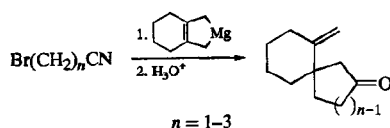


$n-Bu_3SnH/H_2O$ JACS 115 6666 (1993)
JOC 59 7876 (1994)

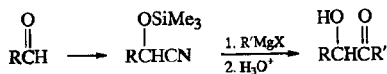
Li, (4-*t*-BuC₆H₄)₂ SL 44 (1991)

t-BuLi/ H_2O JOC 56 550 (1991)

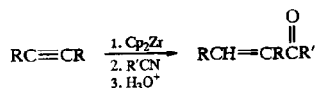
Mg/ H_2O JOMC 87 25 (1975)



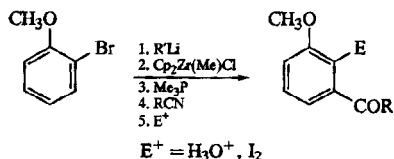
See page 420, Section 2.6.



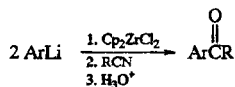
TL 27 1933 (1986)



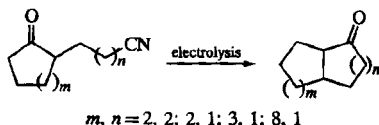
See page 440, Section 2.15.



JACS 109 7137 (1987); 113 258 (1993) (naphthalenes)
 TL 31 5563 (1990); 32 5465 (1991)

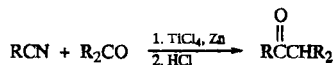


TL 28 3245 (1987)

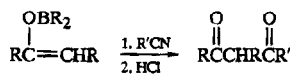


TL 31 1303 (1990)

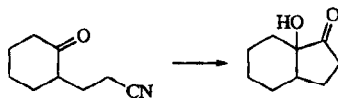
JOC 57 7175 (1992)



TL 34 1617 (1993)

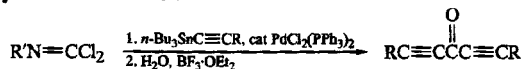


Syn Commun 12 189 (1982)



See page 1176, Section 2.2.

2.18. From Isocyanide Dichlorides



TL 29 5379 (1988)

3. Friedel-Crafts and Related Reactions

Reviews:

Chem Rev 55 229 (1955)

Ind Eng Chem 47 1926 (1955); 48 1670 (1956); 50 1414 (1958); 51 1099 (1959)

- "Friedel-Crafts and Related Reactions," Ed. G. A. Olah, J. Wiley & Sons, New York (1964), Vol 3, Pts 1 and 2
 Syn 533 (1972)
 G. A. Olah, "Friedel-Crafts Chemistry," Wiley Interscience, New York (1973)
 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Parts 3.1-3.3, pp 707-768



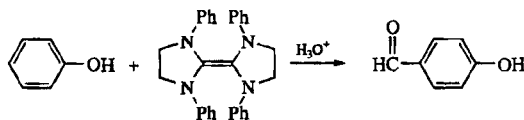
Reviews:

"Friedel-Crafts and Related Reactions," Chpts 32 and 38
 Chem Rev 87 671 (1987)

- | | |
|---|--|
| HCN, HCl, ZnCl ₂ or AlCl ₃ /H ₂ O | Org Rxs 9 37 (1957) (review) |
| NaCN or Me ₃ SiCN, CF ₃ SO ₃ H, cat SbF ₅ | JACS 113 691 (1991); 117 3037 (1995) |
| Me ₃ SiCN, CF ₃ SO ₃ H | JACS 117 3037 (1995) |
| Zn(CN) ₂ , HCl/H ₂ O | TL 23 4567 (1982) |
| Zn(CN) ₂ , AlCl ₃ , HCl/H ₂ O | Org Syn Coll Vol 3 549 (1955)
JOC 52 336 (1987) |
| (CH ₃) ₂ C(OH)CN, AlCl ₃ | Syn Commun 12 485 (1982) |
| CO, HF, SbF ₅ | CC 1551 (1991)
JOC 58 3213 (1993); 60 2106 (1995) |
| CO, HCl, AlCl ₃ | Org Rxs 5 290 (1949) (review) |
| CO, HCl, CuCl/AlCl ₃ | Org Syn Coll Vol 2 583 (1943) |
| CO, HSO ₃ F, SbF ₅ | JOC 57 2677 (1992) |
| CO, CF ₃ SO ₃ H | JCS Perkin I 181 (1980) |
| CO, CF ₃ SO ₃ H, HF, BF ₃ | JOC 50 1483 (1985) |
| CO, CF ₃ SO ₃ H, SbF ₅ | JOC 50 1483 (1985); 60 2106 (1995) |
| FCHO, BF ₃ | JACS 82 2380 (1960) |
| Cl ₂ CHOCH ₃ , AlCl ₃ | Ber 93 88 (1960)
JOC 49 3963 (1984) |
| Cl ₂ CHOR (R = Me, n-Bu), SnCl ₄ | Ber 93 88 (1960)
JOC 60 1448, 1454, 6592 (1995) |
| Cl ₂ CHOCH ₃ , TiCl ₄ | Ber 93 88 (1960); 96 308 (1963)
CC 214 (1972)
Org Syn Coll Vol 5 49 (1973)
JCS Perkin I 340 (1973)
JOC 49 3963 (1984); 50 3121 (1985); 52 1972 (1987); 53 1003 (1988); 56 4312 (1991); 57 3312 (1992); 58 4155 (1993); 60 1448 (1995)
TL 27 6299 (1986) |

$\text{Cl}_2\text{CHO}-n\text{-Bu}$, TiCl_4	Ber 93 88 (1960)
$\text{HC}(\text{OEt})_3$, AlCl_3 (on ArOH)	Ber 96 308 (1963)
$\text{EtOCH} \begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{S} \end{array}$, $\text{BF}_3 \cdot \text{OEt}_2 / \text{H}_3\text{O}^+$	BCSJ 54 2120 (1981)
DMF , POCl_3	Org Syn Coll Vol 4 331 (1963) "Friedel-Crafts and Related Reactions," Vol 3, Pt 2, p 1211 "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 3.5, p 777 (review) SL 77 (1992) JOC 60 5717 (1995)
DMF , $\text{Cl}_2\text{P}(\text{O})\text{OP}(\text{O})\text{Cl}_2$	SL 77 (1992)
DMF , Ti_2O	CC 1571 (1990)
HCONMePh , POCl_3	JOC 60 2964 (1995)
HCONR^1R^2 , $\text{P}_2\text{O}_3\text{Cl}_4$	SL 823 (1994)
HCCl_3 , NaOH (on ArOH)	Org Rxs 28 1 (1982) (review) "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 2, Part 3.4, p 769

$\text{NO}_2\text{-Ar-H} \longrightarrow \text{NO}_2\text{-Ar-CHO}$	
HCCl_3 , $\text{KO}-t\text{-Bu} / \text{H}_2\text{O}$, HCO_2H	TL 28 3021 (1987)
$\text{HC}(\text{SPh})_3$, NaOH , DMSO / hydrolysis	CL 1623 (1984)





Angew Int 11 964 (1972); 15 169 (1976)
Ann 345 (1978)



Review: "Friedel-Crafts and Related Reactions," Chpts 31 and 32

PhCCl_3 , cat zeolite	TL 35 2601 (1994)
RCO_2H , PPA	J Phys Chem 92 6249 (1988)
RCO_2H , $(\text{CF}_3\text{CO})_2\text{O}$	JOC 58 3538 (1993)
RCO_2H , $(\text{CF}_3\text{CO})_2\text{O}$, $\text{CF}_3\text{CO}_2\text{H}$	JOC 59 8220 (1994)
RCO_2H , $(\text{CF}_3\text{CO})_2\text{O}$, H_3PO_4	Syn 303 (1979)
RCOCl , cat $\text{CF}_3\text{SO}_3\text{H}$	Angew Int 11 300 (1972)

RCOCl, Nalfion-H	Syn 672 (1978)
RCOCl, cat zeolite	TL 35 2601 (1994)
RCOCl, AlCl ₃	"Friedel-Crafts and Related Reactions," Vol 3, Pt 1, pp 1-382 (review) Org Syn Coll Vol 6 34 (1988) JOC 59 1574 (1994); 60 7364 (1995)
RCOCl, AlBr ₃	JACS 102 3056 (1980)
RCOCl, SnCl ₄	Monatsh 112 1155 (1981)
RCOCl, cat Sc(OTf) ₃	SL 545 (1994)
RCOCl, cat Fe-montmorillonite	TL 32 1561 (1991)
RCOCl, cat FeCl ₃ , I ₂ , ZnCl ₂ or Fe	Syn 533 (1972)
RCOCl, cat CoCl ₂	TL 32 5179 (1991)
RCOCl, (RCO) ₂ O or CH ₃ C(=CH ₂)O ₂ CR; cat (Ph ₂ B)SbCl ₆ (ArOR)	CL 165 (1986)
(RCO) ₂ O, HF	JOC 56 5955 (1991)
(RCO) ₂ O, H ₃ PO ₄	Org Syn Coll Vol 3 14 (1955)
(RCO) ₂ O, LiClO ₄ , electrolysis	TL 31 3933 (1990)
(RCO) ₂ O, BF ₃ ·SMe ₂	TL 36 4005 (1995)
(RCO) ₂ O, AlCl ₃	Org Syn Coll Vol 1 517 (1941) Ber 115 3436 (1982) Tetr 38 3555 (1982) JACS 109 7122 (1987)
(RCO) ₂ O, cat Sc(OTf) ₃	SL 545 (1994)
(RCO) ₂ O, cat Hf(OTf) ₄ , LiClO ₄ , MeNO ₂	TL 36 409 (1995)
(RCO) ₂ O, ZnCl ₂	Org Syn Coll Vol 2 304 (1943)
(RCO)SbF ₆	Syn 345 (1980)
(RCO)SbF ₆ , CF ₃ SO ₃ H	JACS 117 3037 (1995)
(RCO)SbF ₆ , CF ₃ SO ₃ H, cat SbF ₅	JACS 117 3037 (1995)
RCO ₂ SO ₂ CF ₃	Angew Int 11 299 (1972)
RCO ₂ POX ₂ (X = F, Cl)	Ber 114 926 (1981)
RCO ₂ -  , CF ₃ CO ₂ H	Syn 139 (1980)
RCOSMe, CuOTf	JACS 102 860 (1980)
RCOS- <i>n</i> -Bu, Hg(O ₂ CCF ₃) ₂	TL 31 1977 (1990) (intramolecular)
RCONMe ₂ , POCl ₃	Helv 42 1659 (1959) JOC 25 2049 (1960)
RCON-  , CF ₃ CO ₂ H	BCSJ 53 1638 (1980)

RCN, HCl, $\text{ZnCl}_2/\text{H}_2\text{O}$

Org Syn Coll Vol 2 522 (1943)

Org Rxs 5 387 (1949) (review)

"Friedel-Crafts and Related Reactions," Vol 3, Pt 1,
p 383 (review)

JOC 43 4172 (1978) (intramolecular)

RCN, $\text{CF}_3\text{SO}_3\text{H}$, cat SbF_5

JACS 117 3037 (1995)

$(\text{RC}\equiv\text{NH})\text{OTf}/\text{H}_2\text{O}$

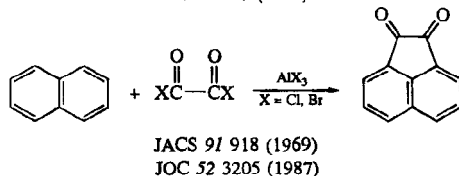
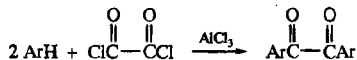
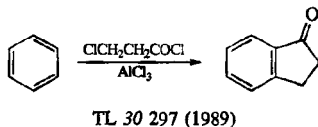
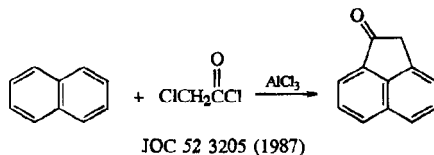
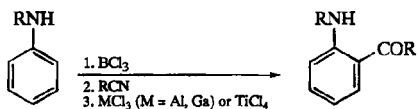
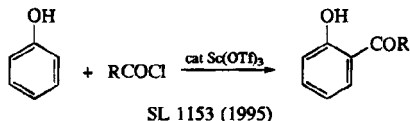
JCS Perkin I 2894 (1980)

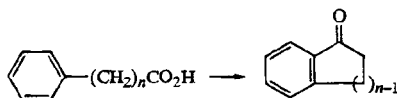
$(\text{RC}\equiv\text{NMe})\text{OTf}/\text{H}_2\text{O}$

CC 1151 (1980)

$(\text{RC}\equiv\text{NMe})\text{OTf}$, $\text{CF}_3\text{SO}_3\text{H}$, cat SbF_5

JACS 117 3037 (1995)



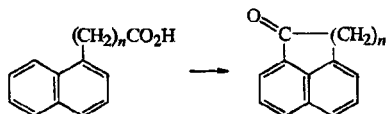


Reviews:

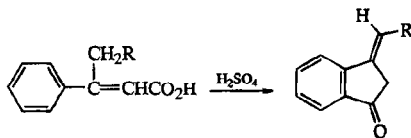
Org Rxs 2 114 (1944)
Angew 66 435 (1954) (PPA)

<u>n</u>	<u>Acid or Lewis Acid</u>	
2	HF	JACS 61 1272 (1939) JOC 56 6717 (1991)
	CH ₃ SO ₃ H	JOC 46 2974 (1981)
	CH ₃ SO ₃ H, P ₂ O ₅	JOC 38 4071 (1973)
	PPA	Helv 29 859 (1946) JACS 72 2965 (1950); 108 1251 (1986) BSCF 810 (1957); II 116 (1982) Compt Rend 246 779 (1958); 249 2337, 2782 (1959) Syn Commun 11 993 (1981) CC 185 (1982) JOC 51 1402, 4250 (1986); 53 904, 3761 (1988); 54 4218 (1989); 58 4398 (1993) TL 30 6603 (1989)
	(CF ₃ CO) ₂ O	Chem Pharm Bull 30 2590 (1982) TL 32 6327 (1991)
	AlCl ₃ , NaCl	JCS 2403 (1953)
	SnCl ₄	JCS 4306 (1954)
3	HF	JACS 61 1272 (1939); 76 3625 (1954) Can J Chem 49 2712 (1971) JCS Perkin I 461 (1982) JOC 52 1284 (1987); 58 4155 (1993); 60 4905 (1995) TL 29 3175 (1988); 30 6603 (1989)
	H ₂ SO ₄	JCS 1125 (1932); 4306 (1954) Tetr 2 271 (1958) JOC 28 3571 (1963) TL 23 2415 (1982)
	H ₂ SO ₄ , B(OH) ₃	JACS 103 4251 (1981)
	CH ₃ SO ₃ H	JOC 46 2974 (1981); 52 5574 (1987); 54 3533 (1989)
	Nalflon-H	JOC 56 3955 (1991)
	CF ₃ CO ₂ H, (CF ₃ CO) ₂ O	Chem Pharm Bull 30 2440 (1982)
	(CF ₃ CO) ₂ O	JCS 1435 (1957)
	POCl ₃	JCS 787 (1939)
	P ₂ O ₅	Tetr 38 3555 (1982)
	P ₂ O ₅ , MeSO ₃ H	JOC 50 5886 (1985); 53 4021 (1988)
	P ₂ O ₅ , H ₃ PO ₄	JOC 55 3537 (1990)
	P ₂ O ₅ , (Me ₃ Si) ₂ O	JOC 54 5642 (1989)
	PPA	JCS 1995 (1938) JACS 69 58 (1947); 72 2965 (1950); 73 1411 (1951); 74 5147 (1952); 78 450 (1956); 103 4251 (1981); 110 497 (1988)

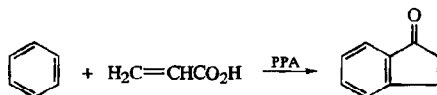
<u>n</u>	<u>Acid or Lewis Acid</u>	
3 (continued)		Org Syn Coll Vol 3 798 (1955) JOC 43 4172 (1978); 46 2547 (1981); 54 5272 (1989); 59 2687 (1994); 60 2714 (1995) BSCF II 116 (1982) TL 30 6603 (1989)
	AlCl ₃ , NaCl	JCS 2403 (1953)
	SnCl ₄	JCS 867 (1934); 790 (1939) JACS 69 58 (1947)
	ZnCl ₂ , HOAc, Ac ₂ O	JACS 69 58 (1947)
4	Nalfion-H	JOC 56 3955 (1991)
	PPA	JACS 73 1411 (1951); 75 720 (1953); 116 9471 (1994) BCSJ 35 1380 (1962) Syn Commun 11 993 (1981) JOC 59 7968, 8220 (1994)
	AlCl ₃ , NaCl	JCS 2403 (1953)
5	PPA	JACS 77 4596 (1955)
9	(CF ₃ CO) ₂ O, CF ₃ CO ₂ H	TL 32 1599 (1991)



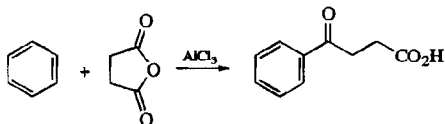
<u>n</u>	<u>Reagent</u>	
1	HF	JOC 44 2158 (1979); 52 1355 (1987); 53 2620 (1988)
	PPA	JCS 4306 (1954)
2	HF	JACS 62 1855 (1940)
2 or 3	H ₂ SO ₄ or PPA or SnCl ₄	JCS 4306 (1954)
3	P ₂ O ₅ or SnCl ₄	JCS 787 (1939)



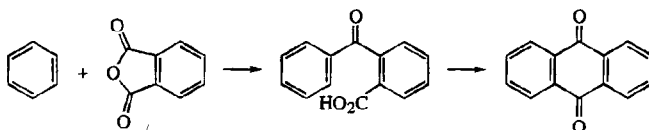
Acta Chem Scand B 36 371 (1982)



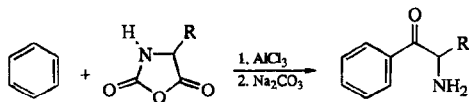
Ind J Chem B 20 241 (1981)



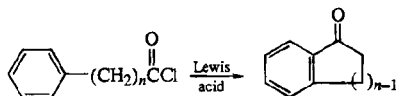
JOC 55 3537, 4971 (1990); 58 4155 (1993); 60 4905 (1995)



Houben-Weyl, Vol VII/3C, p 31 (review)
JOC 52 3205 (1987)



JOC 57 7334 (1992)



n

Lewis acid

2

AlCl₃

Ann 376 269 (1910); 468 277 (1929); 586 52 (1954)

Ber 46 1700 (1913); 55 1835 (1922)

J Prakt Chem [2] 139 95 (1934)

JCS 1460, 3499 (1951)

BSCF 810 (1957)

Tetr 2 271 (1958)

JACS 80 1243 (1958)

Compt Rend 249 2337, 2782 (1959); 252 1971 (1961)

BCSJ 35 1380 (1962)

JOC 46 2431 (1981); 51 5252 (1986); 55 247 (1990)

SnCl₄

Compt Rend 246 779 (1958); 249 2782 (1959)

FeCl₃

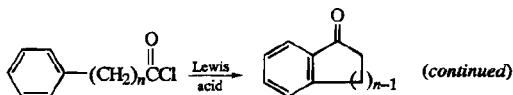
Ann 323 246 (1902)

AgClO₄

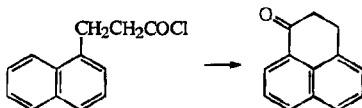
JCS 1718 (1957)

Nalfion-H

JOC 56 3955 (1991)

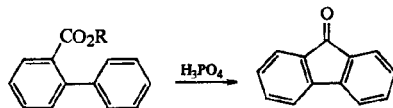


<u>n</u>	<u>Lewis acid</u>	
3	AlCl ₃	JCS 75 144 (1899); 187 (1936); 844, 3499 (1951) Ber 56 1424 (1923); 61 441 (1928) JACS 54 4373 (1932); 110 497 (1988) Ann 531 129 (1937); 586 52 (1954) Org Syn Coll Vol 2 569 (1943) JOC 15 950 (1950); 28 357 (1963) BSCF 190 (1953) Tetr 2 271 (1958)
	SnCl ₄	JACS 57 782 (1935); 59 475 (1937); 62 2750 (1940); 63 1682 (1941); 69 58 (1947) JCS 4306 (1954) Ber 95 1786 (1962) JOC 28 3571 (1963) Org Syn Coll Vol 4 900 (1963)
	TiCl ₄	JACS 113 4931 (1991)
	AgClO ₄	JCS 1718 (1957)
	Nalfion-H	JOC 56 3955 (1991)
4	AlCl ₃	JCS 79 602 (1901) Helv 27 801 (1944) BSCF 769 (1953) JACS 76 3625 (1954) Ann 586 52 (1954) Compt Rend 244 2513 (1957) Tetr 2 271 (1958) J Chem Res (S) 226 (1982) TL 34 6599 (1993)
	AgClO ₄	JCS 1718 (1957)
	Nalfion-H	JOC 56 3955 (1991)
5	AlCl ₃	Ber 85 826 (1952); 90 1946 (1957) JACS 75 3744 (1953); 76 5462 (1954) Ann 586 52 (1954) Tetr 2 271 (1958) BCSJ 35 1380 (1962) J Chem Res (S) 226 (1982)
6, 7	AlBr ₃	Ber 90 1946 (1957)

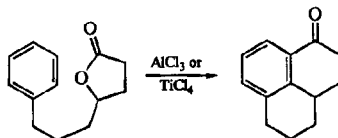
AlCl₃Ber 55 1835 (1922)
JCS 1991 (1938)

SnCl₄

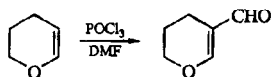
JACS 72 733 (1950)



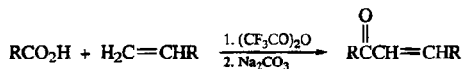
TL 29 2135 (1988)



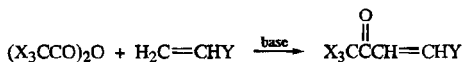
TL 35 4243 (1994)



TL 32 3875 (1991)



JCS 3628 (1953)

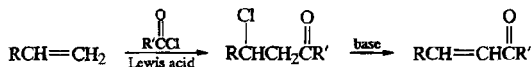
X = F, Cl; Y = OR, SR, NRSO₂R, NRCOR

CL 499 (1976)

TL 1009 (1976); 27 353 (1986)

Syn 1016 (1986)

JOC 60 3523 (1995)



JACS 70 2971 (1948); 108 1265 (1986) (intramolecular)

"Friedel-Crafts and Related Reactions," Vol 3, Pt 2, p 1033 (review)

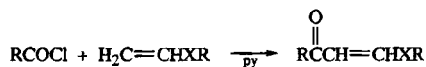
Ind Eng Chem 50 1414 (1958)

JOC 35 858 (1970) (intramolecular); 55 3562, 4403 (1990); 56 713 (1991)

CC 84 (1973) (intramolecular)

TL 2441 (1976); 27 2341 (1986) (intramolecular)

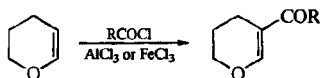
Org Syn Coll Vol 6 883 (1988)



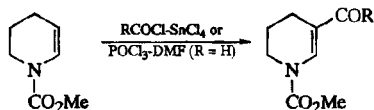
X = O, S

TL 1009 (1976); 27 353 (1986)

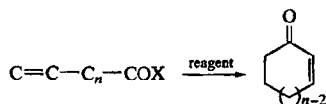
Syn 1016 (1986)



TL 33 7681 (1992)



TL 23 1201 (1982)



X
OH

n
3

Reagent(CF₃CO)₂O

JCS 1435 (1957)

JCS C 217 (1968)

Helv 56 2834 (1973)

PPA

PPA, H₂SO₄

TL 34 5413 (1993)

H₂SO₄

TL 34 5413 (1993)

(CF₃CO)₂O

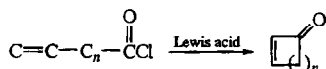
JOC 35 858 (1970)

OR

3

H₂SO₄

TL 34 5413 (1993)

Lewis acid

n

AlCl₃

2

BCSJ 52 216 (1979)

JACS 112 6690 (1990)

SnCl₄

2

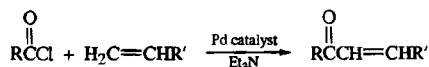
JACS 109 3025 (1987); 117 9804 (1995)

3

JACS 111 2302 (1989); 115 3056 (1993)

4

JOC 35 858 (1970)

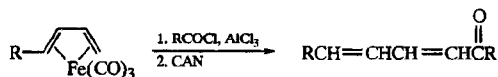


Transition Met Chem 4 398 (1979)

TL 28 4215, 5883 (1987)



TL 28 5949 (1987)



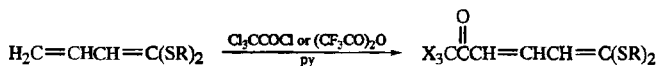
CC 1124 (1969); 373 (1981)

JOMC 122 377 (1976); 166 53 (1979)

Nouv J Chim 14 471 (1990)

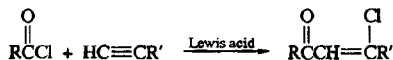
SL 891 (1991)

TL 35 7027 (1994)



X = F, Cl

TL 27 353 (1986)



JOC 1 163 (1936); 29 385 (1964); 50 2796, 4762 (1985); 55 5324 (1990)

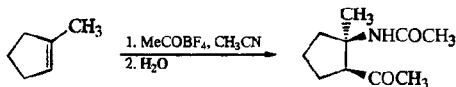
Org Syn Coll Vol 4 186 (1963)

"Friedel-Crafts and Related Reactions," Vol 3, Pt 2, p 1081 (review)

Chem Rev 66 161 (1966) (review)

TL 1821 (1970)

Tetr 29 4241 (1973); 31 177 (1975)



TL 30 1987 (1989)

9. NUCLEOPHILIC ACYLATION

See also page 1451, Section 10, and page 1461, Section 11.

Reviews:

Angew Int 8 639 (1969)

Chem Ind 687 (1974)

Tetr 32 1943 (1976); 36 2531 (1980)

Aldrichimica Acta 14 73 (1981); 15 35 (1982)

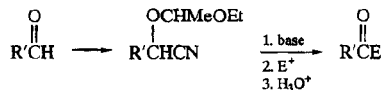
"Advances in the Use of Synthons in Organic Chemistry," Ed. A. Dondoni, JAI Press, Greenwich, CT, Vol 1 (1993)

1. Cyanohydrin Derivatives

Reviews:

Tetr 39 3207 (1983)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 1, Part 2.4, p 541



E^+

$\text{ArH} \cdot \text{Cr}(\text{CO})_3 / \text{I}_2$ ($\text{E} = \text{Ar}$)

JACS 97 1247 (1975); 99 1675 (1977); 101 217 (1979)

Tetr 37 3957 (1981)

Pure Appl Chem 53 2379 (1981) (review)

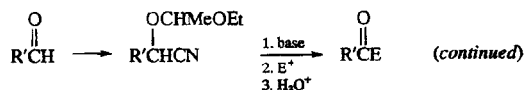
Organomet 2 467 (1983)

$\text{ArX} \cdot \text{Cr}(\text{CO})_3$

JACS 96 7091 (1974)

RX

JACS 93 5286 (1971); 96 5272 (1974); 103 5259 (1981) (intramolecular; $\text{X} = \text{OTs}$; cyclohexanone); 108 4912 (1986); 115 11654 (1993) (intramolecular, 2,9-cycloundecadienone)

 E^+

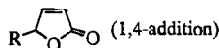
Syn 358 (1973)
 TL 22 1359*, 1363*, 2651*, 3683 (1981); 23 4361* (1982); 24 4683 (1983); 33 7561 (1992); 35 7957 (1994); 36 35* (1995) (* intramolecular)
 JOC 51 3393 (1986) (X = OTs); 54 4273 (1989) (X = OTs); 57 3521 (1992) (all intramolecular)
 SL 121 (1994) (R' = CO₂R)

RCHO, R₂CO

JOC 45 395 (1980)
 Org Syn 63 79 (1984)
 Org Syn Coll Vol 7 381 (1990)
 SL 121 (1994) (R' = CO₂R)

enone (1,4-addition)

TL 22 2175 (1981)



TL 28 3551 (1987)

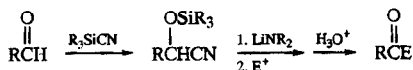
PhCH=CHNO₂ (E = CPh=CH₂)

Syn Commun 10 717 (1980)

H₂C=CMeCH=CHSO_nPh (n = 1, 2;
 1,6-addition)

Syn Commun 11 709 (1981)

RCOCl

SL 121 (1994) (R' = CO₂R)

E⁺ = RX; RCHO; R₂CO; RCOCl; enone; α,β-unsaturated esters; Michael acceptors; R₃SiCl

R

alkyl

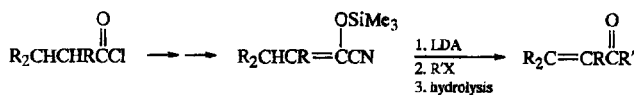
JOC 57 1202 (1992)

aryl

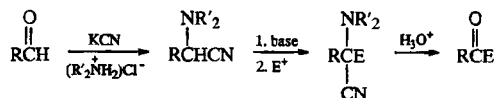
Syn 777 (1973); 180, 391 (1975)
 Ber 112 2045, 2062 (1979); 113 302, 324 (1980)
 Tetr 39 841 (1983)
 JOC 52 564 (1987); 54 1236 (1989); 60 1148, 4585 (1995)
 TL 31 5487 (1990); 33 4473 (1992); 36 1455, 7271 (1995)
 SL 895 (1994)

vinylic

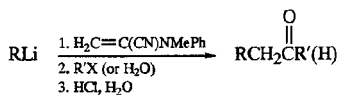
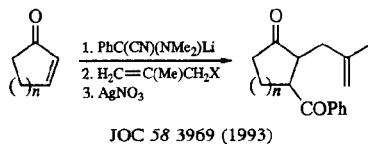
Syn 777 (1973)
 JOC 44 462 (1979); 45 395 (1980); 52 4135 (1987); 59 2700 (1994)
 Ber 113 3783 (1980); 114 959 (1981)
 Syn Commun 11 709 (1981)
 JACS 106 718 (1984); 115 9842 (1993) (intramolecular); 117 8258 (1995) (intramolecular)
 TL 27 5359 (1986); 31 3317 (1990) (intramolecular)



Ber 119 722, 1772 (1986)



R	E ⁺	
H	RX	Heterocycles 19 481 (1982)
	enone (1,4-addition)	Heterocycles 19 1395 (1982)
alkyl	RX	BSCF 1653 (1961)
		Syn 127 (1979)
		JCS Perkin II 1645 (1982)
		TL 23 3369 (1982); 24 4683 (1983); 27 1569 (1986)
	RX, epoxide, H ₂ C=CHCOCH ₃ (1,4-addition)	TL 5175 (1978)
	RCHO, R ₂ CO	CL 71 (1980)
		TL 23 639 (1982)
	RCH=CRCO ₂ R (1,4-addition)	Z Chem 21 68 (1981)
aryl	D ₂ O	CC 218 (1967)
		JCS C 2049 (1970)
	RX	JACS 82 1786 (1960)
		JOC 26 4740 (1961); 48 1909 (1983); 54 3985 (1989); 60 588 (1995)
		Tetr 31 1219 (1975)
		Syn 127 (1979)
		TL 24 4683 (1983)
		JOC 44 4597 (1979)
	RX, RCOCl, epoxide, H ₂ C=CHCN(CO ₂ R) (1,4-addition)	
	enone (1,4-addition)	TL 25 4641 (1984); 27 2985 (1986) (added Lewis acids)
		JOC 51 1293 (1986)
		SL 837 (1992) (chiral)
		JOC 37 4465 (1972)
		JACS 98 6321 (1976)
		J Heterocyclic Chem 15 881 (1978)
		CL 399 (1979)
vinyllic	RX	CL 1263 (1982)
	R ₂ CO	TL 21 1205 (1980)
hydrolysis	H ₂ O, CuSO ₄	TL 2763 (1978)

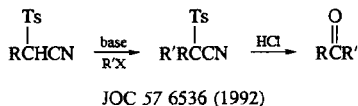
R

alkyl

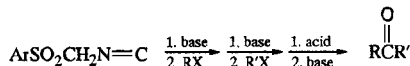
Syn 897 (1978)

enolate or imine anion

Syn 413 (1980)



2. Isonitriles



TL 4229 (1977); 5335 (1982) (cyclophanes); 28 3825 (1987)

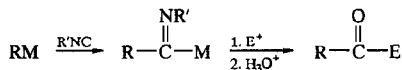
Syn 325 (1980)

JOC 46 5159 (1981); 51 1551 (1986)

Syn Commun 13 331, 379, 1067 (1983)

Chem Pharm Bull 31 2868 (1983)

JACS 107 5238 (1985); 114 10775 (1992)

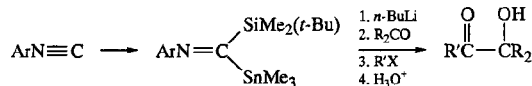
M = Li, MgX; R' = Me₃CCH₂CM₂; E⁺ = H₂O, D₂O, ClSiMe₃, RCHO, epoxide, CO₂,ClCO₂Et, RX (R = 1° alkyl, aryl, alkynyl, vinylic), H₂C=CHCO₂Et (1,4-addition)

JACS 91 7778 (1969); 92 6675 (1970)

JOC 39 600 (1974); 46 5405 (1981); 47 52 (1982)

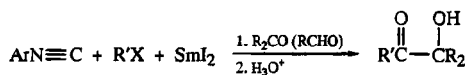
Org Prep Proc Int 11 293 (1979) (review)

Org Syn Coll Vol 6 751 (1988)



Ar = 2,6-xylyl

JACS 109 7888 (1987)



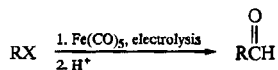
Ar = 2,6-xylyl

JOC 58 1458 (1993)

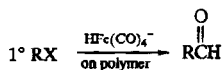
SL 511 (1993)

3. Iron Carbonyl Reagents

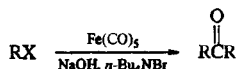
Review: Acct Chem Res 8 342 (1975)



TL 30 6371 (1989)

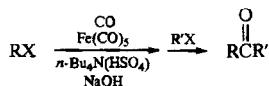


JOC 43 1598 (1978)

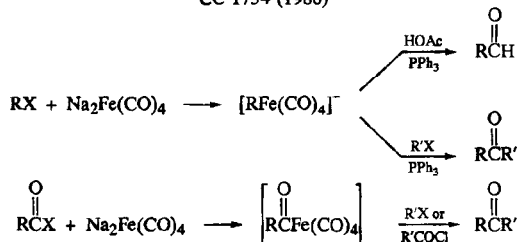


R = 1° alkyl, benzylic

CL 321 (1979)



CC 1754 (1986)

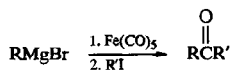


JOC 35 4183 (1970)

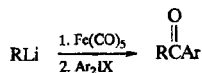
JACS 92 6080 (1970); 94 1788, 5905 (1972); 95 249, 2689 (1973); 99 2515 (1977); 100 4766 (1978)

Org Syn 59 102 (1980)

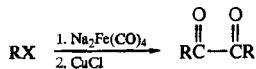
Org Syn Coll Vol 6 807 (1988)



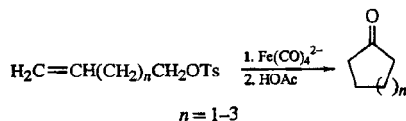
TL 761 (1978)



TL 1255 (1979)

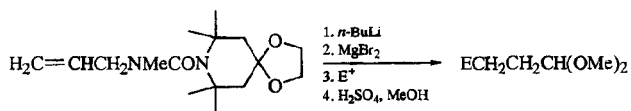


TL 33 1227 (1992)



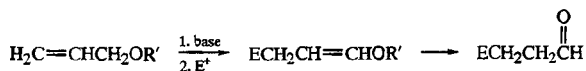
TL 2/ 4687 (1980)

4. Allylic Amides

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}$

Angew 18 399 (1979)

5. Allylic Ethers and Carbamates

R'

alkyl

E⁺

RX

JACS 96 5560 (1974)

TL 833 (1979)

CL 1637 (1982) (chiral)

TL 2115 (1976)

RX, epoxide (intramolecular)

SiR₃

RX

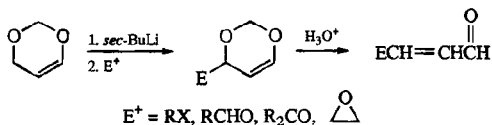
JACS 96 5561 (1974)

SL 686 (1993)

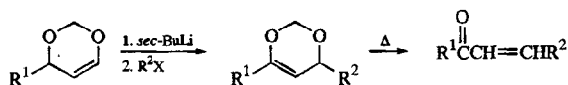
SL 686 (1993)

RCHO, R₂CO

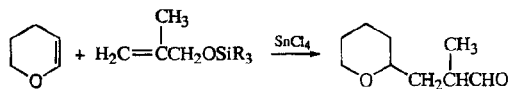
CONR ₂	review	Angew Int 23 932 (1984)
CONMe ₂	(MeO) ₂ CO, RX	Angew Int 19 625 (1980)
CON(<i>i</i> -Pr) ₂	RCHO, R ₂ CO	Angew Int 20 1024 (1981); 21 372 (1982); 25 160 (1986)
	(<i>i</i> -PrO) ₃ TiCl / RCHO	TL 27 4873 (1986); 28 5149 (1987)
	(<i>i</i> -PrO) ₄ Ti / RCHO	TL 28 5149 (1987) SL 611 (1991)
	(Et ₂ N) ₃ TiCl / RCHO	Angew Int 25 160 (1986) TL 28 5149 (1987)
CONHR'	RX, Me ₃ SiCl, (MeS) ₂ , (MeO) ₂ CO	Angew Int 20 127 (1981)



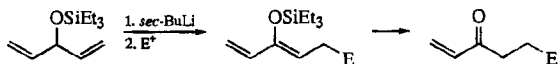
JACS 110 1290 (1988)



TL 29 1111 (1988)



JOC 52 5691 (1987)

 $E^+ = \text{H}_2\text{O}, \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCOCl}, \text{Me}_3\text{SiCl}, (\text{MeS})_2$

TL 4187 (1976)

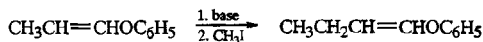
Helv 63 967 (1980); 64 2002, 2022, 2592 (1981)

JACS 104 5708 (1982)

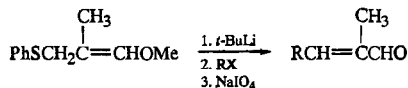
SL 686 (1993) (Ba reagent)

6. Vinylic Ethers

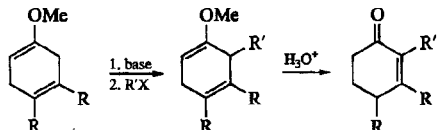
See also page 1440, Section 5.



Helv 57 2261 (1974)



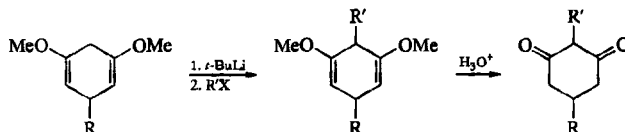
TL 29 2979 (1988)



JCS Perkin I 7 (1983)

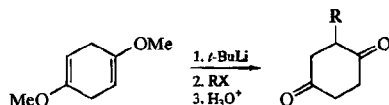
TL 28 4195 (1987)

JACS 115 8873 (1993)

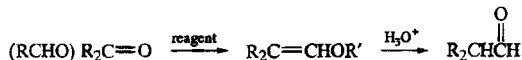


JOC 42 3755 (1977); 47 20, 1576 (1982); 51 1407 (1986)

TL 28 4163 (1987)



JOC 54 840 (1989); 60 6123 (1995)



Review: Org Rxs 14 270 (1965)

Reagent(s) $\text{Ph}_3\text{P}=\text{CHOMe}$

JACS 80 6150 (1958)

Angew 71 127 (1959)

Ber 94 1373 (1961)

JOC 35 1385 (1970); 50 2668, 2676 (1985);

51 2162 (1986); 56 2122 (1991)

Syn 604 (1973)

TL 3979 (1973); 22 1063 (1981)

Tetr 31 89 (1975)

 $\text{Ph}_3\text{P}=\text{CHO}-n\text{-Bu}$

Ber 95 2526 (1962)

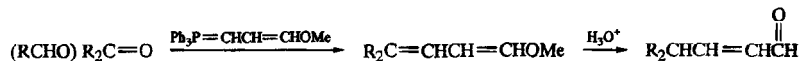
$\text{Ph}_3\text{P}=\text{CHOCH}_2\text{CH}=\text{CH}_2$	JACS 92 5522 (1970)
$\text{Ph}_3\text{P}=\text{CHOAr}$	Ber 95 2514 (1962)
$\text{Ph}_3\text{P}=\text{CHOCH}_2\text{OCH}_3$	Tetr 31 89 (1975)
$\text{Ph}_3\text{P}=\text{CHOTHP}$	Tetr 31 89 (1975)
$(\text{EtO})_2\text{PO}\dot{\text{C}}\text{HOCH}_2\text{CH}_2\text{OCH}_3$	TL 3629 (1978) JOC 44 4847 (1979)
$(\text{RO})_2\text{PO}\dot{\text{C}}\text{HOTHP}$ (R = Et, <i>n</i> -Bu)	TL 3629 (1978) JOC 44 4847 (1979)
$\text{Ph}_2\text{PO}\dot{\text{C}}\text{HOCH}_3$	CC 314 (1977) JCS Perkin I 3099 (1979) CL 1143 (1982) JOC 57 6861, 7143 (1992); 59 406 (1994)
$\text{Ph}_2\text{P}\dot{\text{C}}\text{HOCH}_3$	TL 21 3535 (1980)
$(\text{MeO})_2\text{POCHN}_2$, R'OH, KO- <i>t</i> -Bu	TL 21 2041, 5003 (1980)
$m\text{-CF}_3\text{C}_6\text{H}_4\text{SeCH}(\text{Li})\text{OCH}_3$ / MsCl, Et ₃ N	JACS 101 6638 (1979)
$\text{Me}_3\text{SiCH}(\text{Li})\text{OCH}_3$	CC 822 (1979) Organomet 1 553 (1982)

Reagent

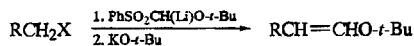
$(n\text{-BuO})_2\text{PO}\dot{\text{C}}(\text{CH}_3)\text{OTHP}$	TL 3629 (1978)
$\text{Ph}_2\text{PO}\dot{\text{C}}(\text{CH}_3)\text{OCH}_3$	CC 314 (1977) JCS Perkin I 3099 (1979)



CL 967 (1981)
JOC 49 3595 (1984)



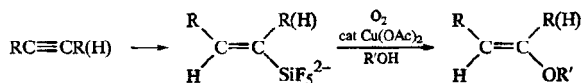
TL 3875 (1977)



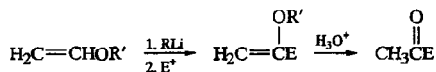
SL 505 (1991)



See page 931, Section 1.

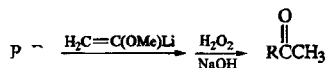


TL 21 4105 (1980)



$\text{R}' = \text{Me, Et, THP}; \text{E}^+ = \text{RX, RCHO, R}_2\text{CO, RCO}_2\text{Me, RCN}$

See page 351, Section 1.



JOMC 156 123 (1978)



RX

ArBr(I) JOC 46 5414 (1981); 57 1481 (1992)

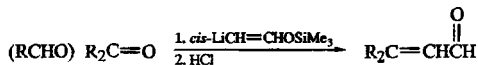
ArOTf JOC 55 3654 (1990); 57 1481, 3558 (1992); 58 7421 (1993); 60 3249 (1995)
SL 871 (1992)

ArCOCl (R = Ar) JOC 57 1481 (1992)

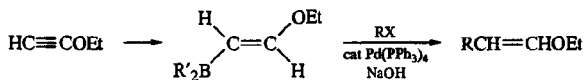
vinyl triflate JOC 54 1502 (1989)



JOC 55 5757 (1990)

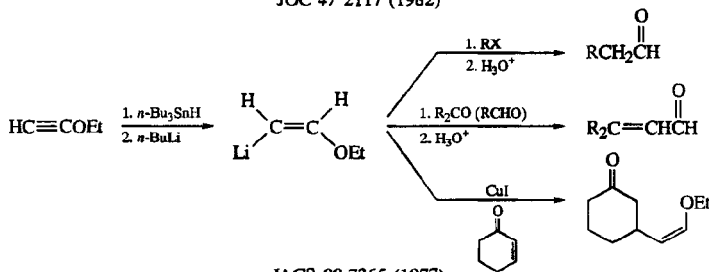


JOMC 46 3741 (1981)



R = aryl, benzylic

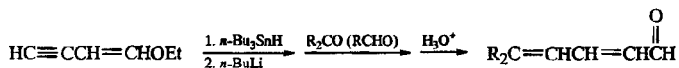
JOC 47 2117 (1982)



JACS 99 7365 (1977)

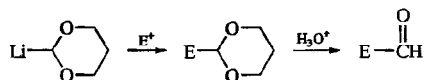
TL 3589 (1977)

JOC 43 1595 (1978)



TL 717 (1978)

7. Other Metallated Ethers



$\text{E}^+ = \text{RX}, \text{Me}_2\text{SO}_4, \text{epoxide}, \text{RCHO}, \text{R}_2\text{CO}, \text{enone (plus CuI}\cdot\text{PBu}_3 \text{ and BF}_3\cdot\text{OEt}_2, \text{1,4-addition)}$

JACS 111 1381 (1984)



$\text{E}^+ = \text{R}'\text{X}, \text{Me}_2\text{SO}_4, \text{RCHO}, \text{R}_2\text{CO}, \text{Me}_3\text{SiCl}$

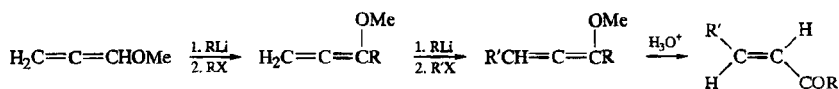
Rec Trav Chim 87 916 (1968)

TL 2585 (1973)

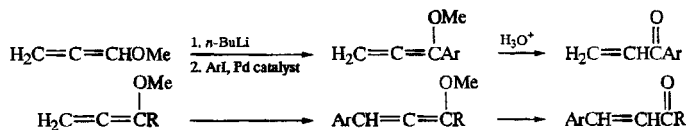
Angew Int 18 875 (1979)

JACS 104 1119 (1982); 106 5360 (1984)

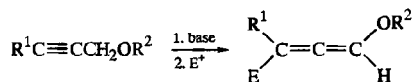
JOC 57 1179 (1992)



TL 1137 (1978)



Syn 738 (1982)

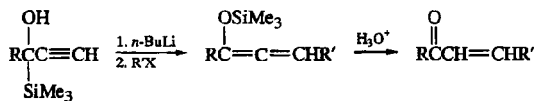


$\text{E}^+ = \text{H}_2\text{O}, \text{RX}, \text{R}_2\text{SO}_4, \text{Me}_3\text{SiCl}$

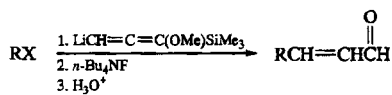
TL 2585 (1973)

Angew Int 18 875 (1979)

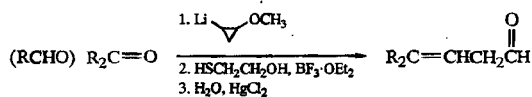
JOMC 232 C1 (1982)



TL 28 1299 (1987)

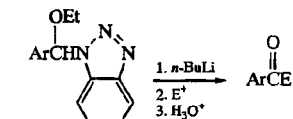


TL 21 3987 (1980)

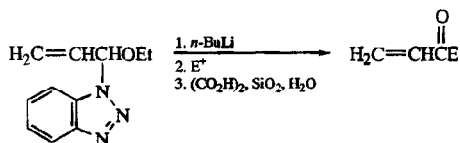


TL 3685 (1975)

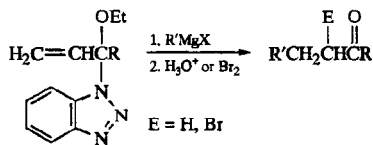
8. Amino Acetals

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCH}=\text{NR}$

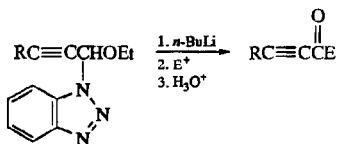
JOC 60 7619 (1995)

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{H}_2\text{C}=\text{CHCOR}$ (1,4-addition), $\text{H}_2\text{C}=\text{CHCO}_2\text{R}$ (1,4-addition)

JOC 60 7589, 7597 (1995)

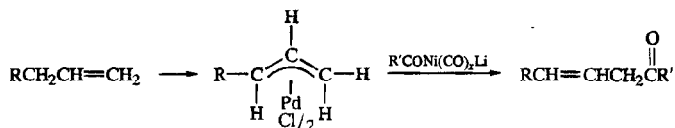


JOC 60 7605 (1995)

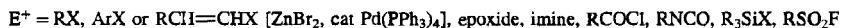
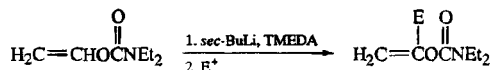


JOC 60 7612 (1995)

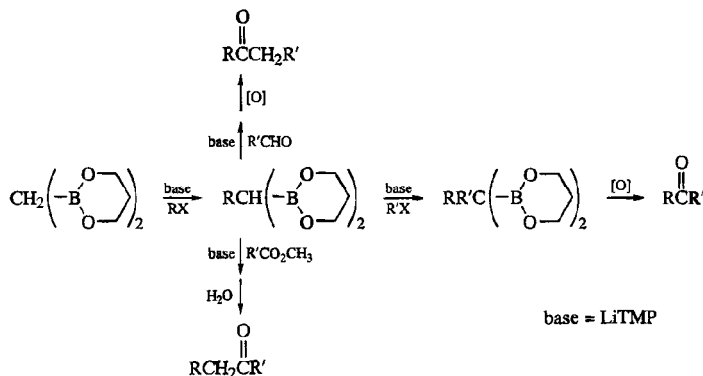
9. Miscellaneous Nucleophilic Acylation Reactions



Organomet 1 1188 (1982)

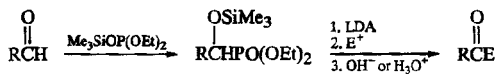


JOC 55 5680 (1990)



JACS 97 5608 (1975); 99 3196 (1977)

Organomet 1 20, 280 (1982)

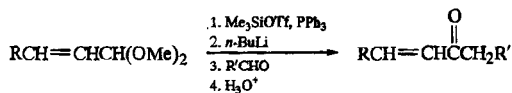
 E^+

RX

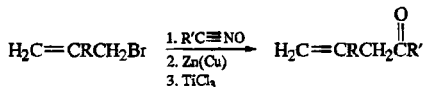
BCSJ 55 224 (1982)

RCOCl

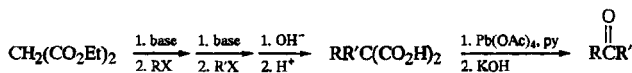
JOC 56 902 (1991)



TL 31 2901 (1990)

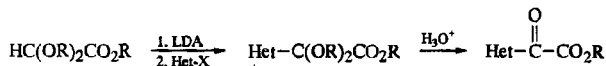


Angew Int 18 78 (1979)

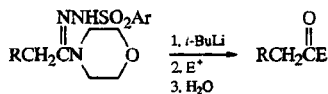
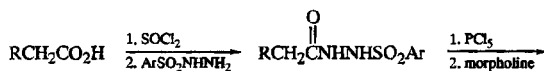


TL 6145 (1966)

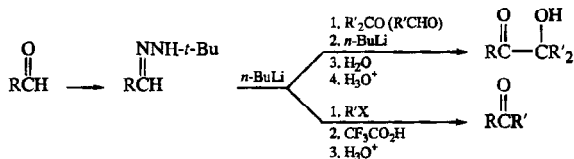
Org Rxs 19 279 (1972) (decarboxylation review)



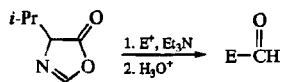
TL 27 6059 (1986)

 $\text{E}^+ = \text{MeI}, \text{R}_2\text{CO}$

CC 1121 (1981)



CC 1040 (1983)



$E^+ = H_2C=CHX$ ($X = CHO, COR, CO_2R, NO_2$; 1,4-addition), $RCHO$

TL 34 3907 (1993)

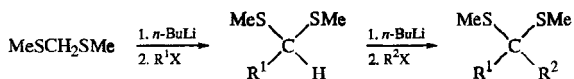
10. SULFUR, SELENIUM AND TELLURIUM REAGENTS

See also page 1461, Section 11.

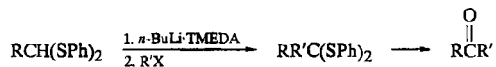
Review: Syn 357 (1977)

1. Sulfur Acetals

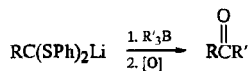
Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 1, Part 2.4, p 541



TL 23 1047 (1982)

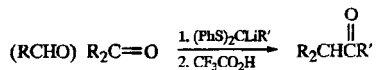


TL 21 4763 (1980)

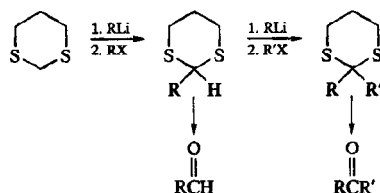


CL 961 (1973)

TL 1893 (1979)



CC 547 (1976)



Angew Int 7 619, 620 (1968)

Syn 1 17 (1969); 357 (1977); 561 (1980) (hydrolysis); 135 (1981) (hydrolysis); 580, 679 (1982) (both hydrolysis)

JOC 36 366, 3553 (1971); 40 231 (1975); 46 1512 (1981); 47 1145, 2212 (hydrolysis) (1982)

CC 529 (1972); 255 (1978) (hydrolysis)

JACS 98 6387 (1976); 99 1675 (1977); 101 217, 3535 (1979); 103 3112 (1981); 111 6648 (1989); 112 6942, 8465 (1990)

Heterocycles 6 731 (1977)

JCS Perkin I 1036 (1978)

Syn Commun 11 343 (1981)

Tetr 37 3957 (1981); 45 7643 (1989) (review)

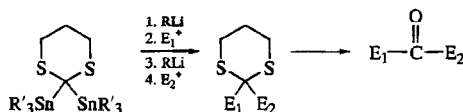
JOMC 240 C5 (1982)

Ann 1589 (1982)

Organomet 2 467 (1983)

TL 27 2965 (hydrolysis), 6305 (alternate preparation) (1986); 29 5937, 5939 (1988); 30 287 (1989) (hydrolysis); 31 7261 (1990) (metallation)

Org Syn Coll Vol 6 316 (1988)



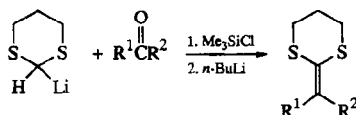
R' = Me, n-Bu

E₁⁺, E₂⁺ = RX, RCHO; RX, epoxide; RCHO, -; R₂CO, -; RCO₂R, -; (RCO)₂O, -

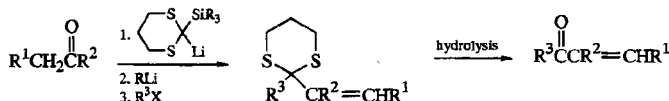
Helv 61 2510 (1978)

TL 30 15 (1989)

JACS 112 4552 (1990)



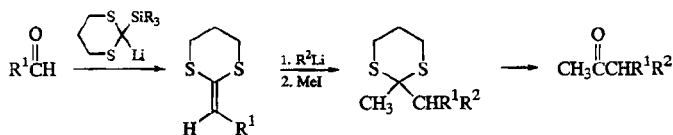
Syn 579 (1982)



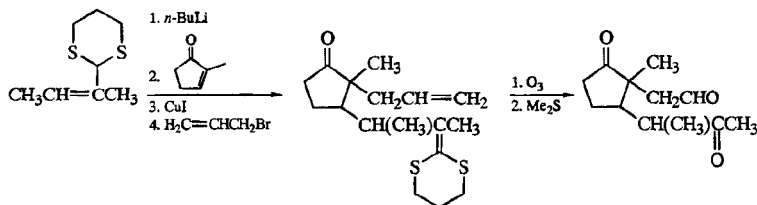
TL 3171 (1974)

Ann 811 (1977)

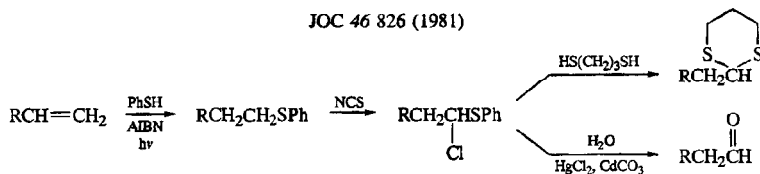
JCS Perkin I 2678 (1980)



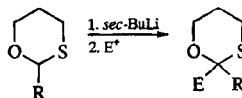
Ann 830 (1977)



JOC 46 826 (1981)



Syn Commun 6 575 (1976)

 E^+

RX

CC 814 (1977)

TL 33 725 (1992)

epoxide

JACS 103 3112 (1981)

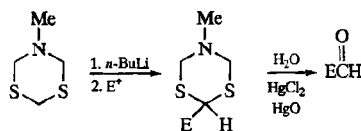
RCHO

JACS 106 2937, 2943 (1984)

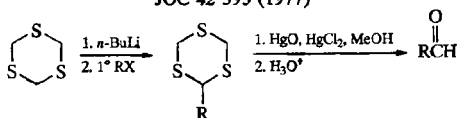
TL 33 725 (1992)

Me_3MCl (M = Si, Ge, Sn), Me_3PbOAc or $(\text{MeX})_2$
(X = S, Se)

TL 22 2005 (1981)

 $\text{E}^+ = \text{RX, RCHO, R}_2\text{CO}$

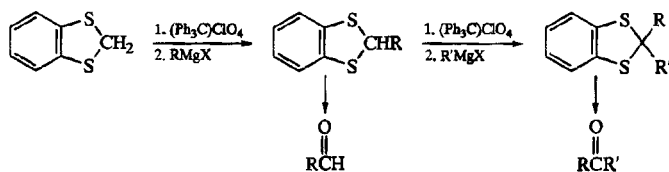
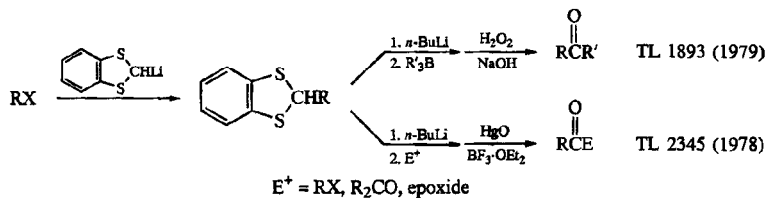
JOC 42 393 (1977)



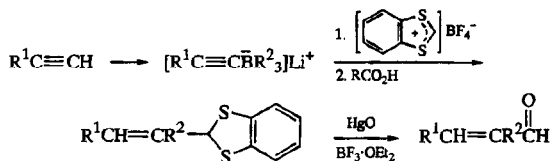
Syn 17 (1969)

Org Syn 51 39 (1971)

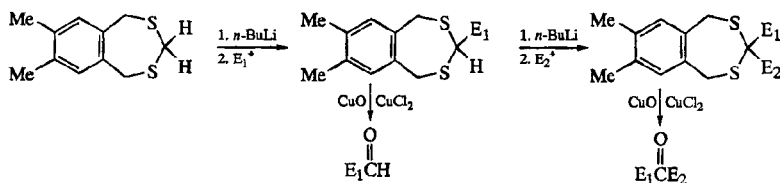
Org Syn Coll Vol 6 869 (1988)



JCS Perkin I 1886 (1976)
TL 22 1821 (1981)

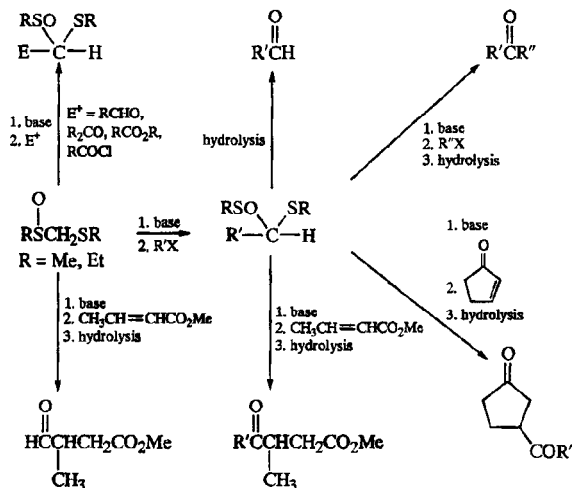


CC 164 (1981)



$\text{E}_1^+ = \text{RX}; \text{E}_2^+ = \text{RX}, \text{epoxide}$

JCS C 1005 (1966)
TL 1837 (1972)
Syn 720 (1975)

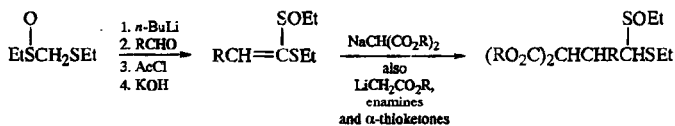
2. α -Thioisulfoxides

TL 3151 (1971); 3267, 3271, 3275, 4707 (1973); 3653 (1974); 2767 (1975); 1303 (1978); 27 6381 (1986)

Syn 117 (1974)

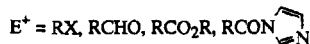
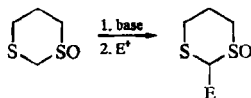
JOC 52 5466 (1987); 60 7548 (1995)

JACS 117 9804 (1995)

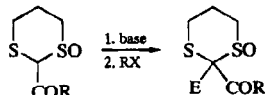


TL 4707, 4711, 4715 (1973)

JACS 96 3701 (1974)

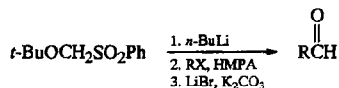


TL 34 5159, 6947 (1993)

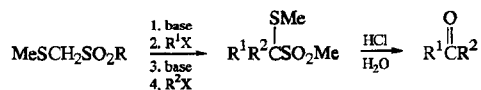
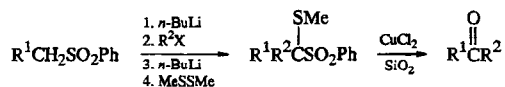


JCS Perkin I 185, 2441 (1989)

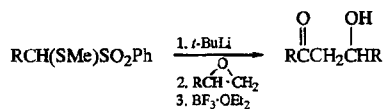
TL 34 6947 (1993)

3. α -Substituted Sulfones

SL 501 (1991)

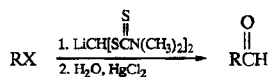
CL 813 (1982) (R = Me); 767 (1983) (R = *p*-Tol)

BCSJ 56 2539 (1983)

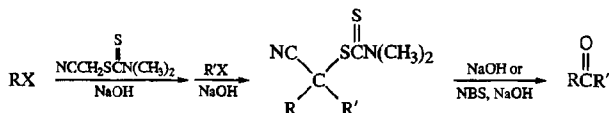


TL 35 2091 (1994)

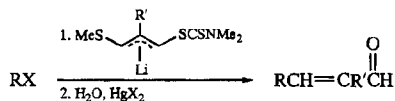
4. Thiocarbamates



CL 731 (1974)

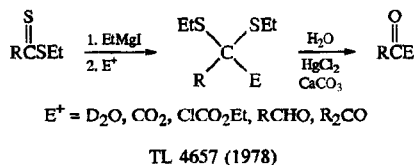


TL 2967 (1976)



TL 3625 (1974)

5. Thioesters

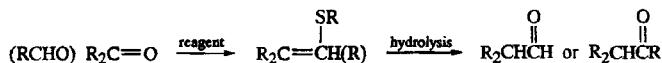


6. Vinylic and Allylic Sulfides and Selenides

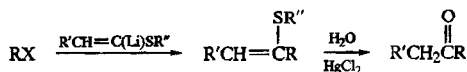
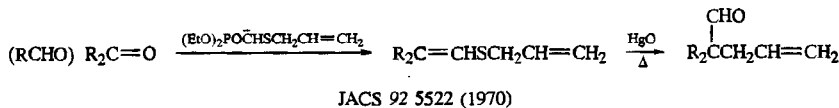
Reviews:

TL 4437 (1975) (hydrolysis of vinylic sulfides)

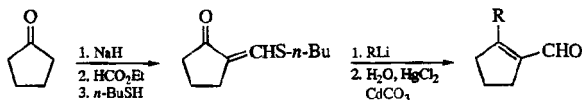
Syn 357 (1977)

Reagent

$\text{Ph}_3\text{P}=\text{CHSMe}$	Ber 94 1373 (1961)
$\text{Ph}_3\text{P}=\text{CHS}-n\text{-Bu}$	TL 3787 (1968)
$\text{Ph}_3\text{P}=\text{CHSPh}$	TL 3665 (1969); 4451 (1974)
$\text{Ph}_3\text{P}=\text{CHSR}$ ($\text{R} = \text{Ph}, \text{PhCH}_2, n\text{-Pr}$)	Ann 2085 (1974)
$\text{Ph}_3\text{P}=\text{C}(\text{CH}_3)\text{SPh}$	TL 3787 (1968)
$(\text{MeO})_2\text{PO}\bar{\text{C}}\text{HSMe}$	Syn 170 (1969)
$(\text{EtO})_2\text{PO}\bar{\text{C}}\text{HSMe}$	JCS 1324 (1963)
	Syn 278 (1975)
	JOC 40 1979 (1975)
$(\text{EtO})_2\text{PO}\bar{\text{C}}\text{HSAr}$	Syn 145 (1970); 278 (1975)
$(\text{EtO})_2\text{PO}\bar{\text{C}}\text{RSMe}$	JOC 35 777 (1970); 44 2967 (1979)
	JCS Perkin I 1879 (1974)
$\text{Ph}_2\text{PO}\bar{\text{C}}\text{RSR}$	JCS Perkin I 2263 (1977)
$\text{Me}_3\text{SiCH}(\text{Li})\text{SPh}$	TL 22 2803 (1981)



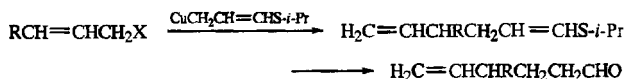
JACS 95 2694 (1973)



TL 1015 (1979)

 $\text{E}^+ = \text{R}'\text{X}, \text{epoxide}, \text{R}_2\text{CO}, \text{R}_3\text{SiCl}$

Ber 110 1833 (1977)



JACS 95 7926 (1973)

R' Reagents

H	$\text{MeS}\bar{\text{C}}\text{HCH}=\text{CHSMe} / \text{H}_2\text{O}, \text{HgCl}_2$	TL 311 (1970) JACS 93 1724 (1971) BCSJ 48 1567 (1975) JOC 41 2506 (1976); 60 4617 (1995)
	$\text{PhS}\bar{\text{C}}\text{HCH}=\text{CHOMe} / \text{H}_2\text{O}, \text{HCl}, \text{HgCl}_2$	CL 345 (1977)
	$\text{PhSe}\bar{\text{C}}\text{HCH}=\text{CHSePh} / \text{H}_2\text{O}_2$	JOC 47 1618 (1982)
Me	$\text{PhSe}\bar{\text{C}}\text{HCH}=\text{CClCH}_3 / \text{H}_2\text{O}_2, \text{py}$	JOC 40 2570 (1975)

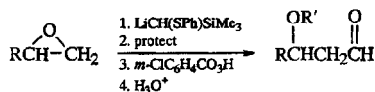
7. Miscellaneous Reactions



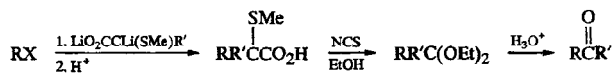
$\text{Me}_3\text{Si}\bar{\text{C}}\text{HSPH} / m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H} / \text{H}_3\text{O}^+$ TL 21 1559, 1677 (1980); 22 2803 (1981)
JCS Perkin I 1131 (1983)

$\text{Me}_3\text{Si}\bar{\text{C}}\text{HSePh} / \text{H}_2\text{O}_2$ TL 4223 (1976)

$\text{LiCH}(\text{TePh})_2 / \text{NaI}, \text{I}_2$ CL 1081 (1982)



TL 21 1559 (1980); 27 4403 (1986)



TL 3797 (1975)

JACS 97 3529 (1975)

Chem Rev 78 363 (1978) (review)

Acct Chem Res 11 453 (1978) (review)



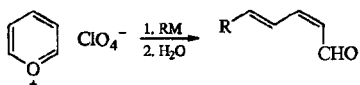
TL 1007 (1975)

11. HETEROCYCLES

Review: Heterocycles 6 731 (1977)

See also page 721, Section 10.

1. Pyrylium Salts



$\text{RM} = \text{RLi}$ ($\text{R} = \text{alkyl, aryl, vinylic, alkynyl}$), RMgX , $(\text{RCH}=\text{CHAlR}_3)\text{Li}$, Ar_4Ti

CC 782 (1985)

JCS Perkin I 683 (1989)

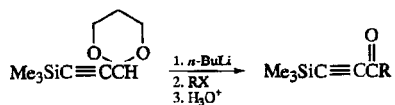
J Chem Res (S) 162 (1990)

TL 31 5843 (1990)

Syn 320 (1991)

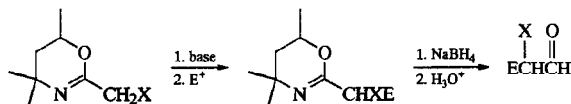
SL 117 (1992)

2. 1,3-Dioxanes



Tetr 39 3073 (1983)

3. 5,6-Dihydro-4H-1,3-oxazines



X = H, R, F, Cl; E⁺ = RX, RCHO, R₂CO, epoxide

CC 1163 (1967)

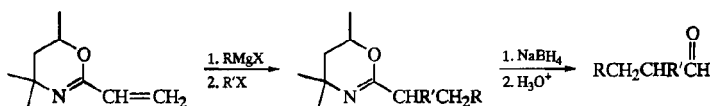
JACS 91 763, 764, 765, 2155 (1969)

Org Prep Proc Int 1 193 (1969)

JOC 38 36 (1973); 39 618 (1974); 43 2907 (1978)

Org Syn Coll Vol 6 905 (1988)

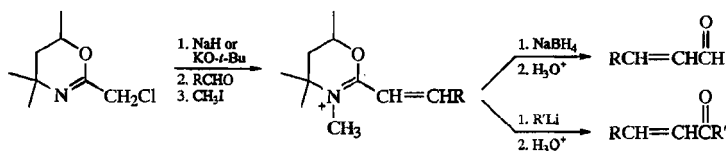
TL 31 179 (1995)



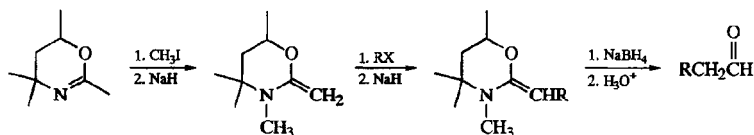
TL 1783, 4809 (1969)

Org Prep Proc Int 1 213 (1969)

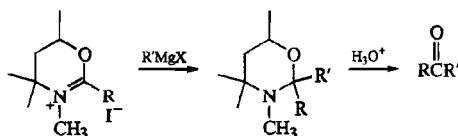
JOC 38 36, 2136 (1973)



JOC 39 623 (1974)

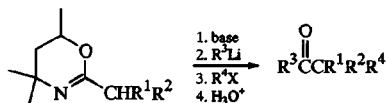


JACS 94 3243 (1972)



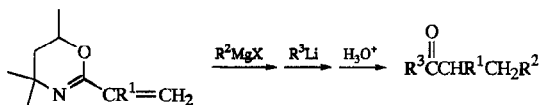
JACS 92 1084 (1970)

JOC 37 4289 (1972); 38 175 (1973)



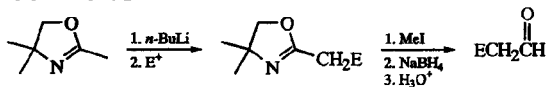
JACS 93 2314 (1971)

JOC 38 2129 (1973)



JOC 38 2136 (1973)

4. 4,5-Dihydrooxazoles

 $E^+ = RX, R_2CO, \text{epoxide}$

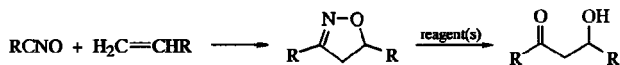
J Heterocyclic Chem 3 531 (1966)

Tetr 29 3417 (1973)

BSCF 2673 (1973)

Pure Appl Chem 51 1255 (1979)

5. 4,5-Dihydroisoxazoles



Reagent(s)

H₂, Raney Ni, MeOH, HOAc

Syn 757 (1980)

Tetr 41 3511 (1985)

H₂, Raney Ni, MeOH, HOAc, H₂O

JOC 55 4668 (1990)

H₂, Raney Ni, EtOH, HOAc

Heterocycles 19 357 (1982)

H₂, Raney Ni, B(OH)₃, MeOH, H₂O

JACS 104 4023, 4024 (1982); 105 5826 (1983)

JOC 55 4585 (1990); 58 2173 (1993); 59 813 (1994)

TL 34 8465 (1993); 35 9749 (1994)

H₂, Raney Ni, B(OMe)₃, MeOH, H₂O

JOC 55 4497 (1990); 56 5281 (1991)

H₂, Raney Ni, BF₃·OEt₂, EtOH, H₂O

TL 24 1337 (1983)

H₂, Raney Ni, AlCl₃, MeOH, H₂O

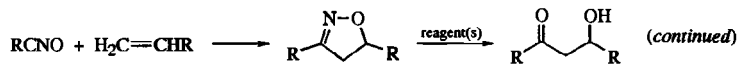
TL 23 3123 (1982)

H₂, cat Pd-C, EtOH, HOAc, H₂O

TL 22 735 (1981)

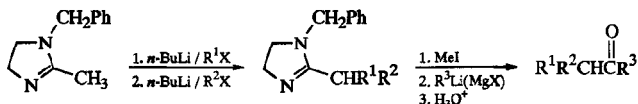
O₃/Me₂S

TL 23 3123 (1982)

Reagent(s)

$\text{CF}_3\text{CO}_3\text{H}$ or $3,5-(\text{NO}_2)_2\text{C}_6\text{H}_3\text{CO}_3\text{H}$, $(\text{Na}_2\text{HPO}_4)$ JOC 55 4668 (1990)

TiCl_3 , MeOH Acta Chem Scand B 36 1 (1982)

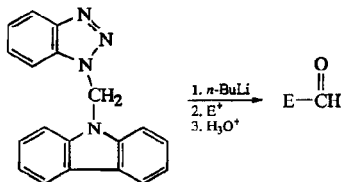
6. 4,5-Dihydro-1H-imidazoles

TL 22 261 (1981)

CC 282 (1982)

7. Benzotriazoles

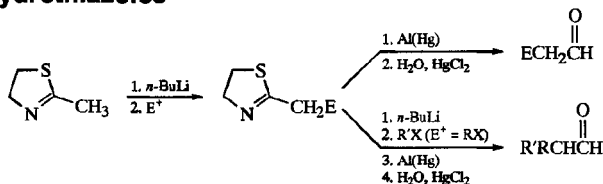
See also page 1446, Section 8.



$\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCO}_2\text{R}, \text{RNCO}, \text{RNCS}, \text{ClCO}_2\text{R}, \text{RSSR}$

J Heterocyclic Chem 26 829 (1989)

JOC 56 2143, 6917 (1991)

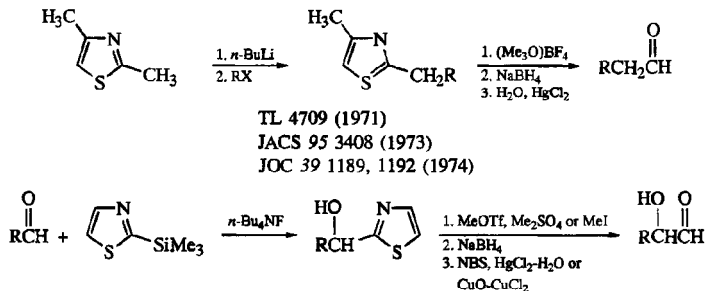
8. 4,5-Dihydrothiazoles

$\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{epoxide}$

TL 3929 (1972)

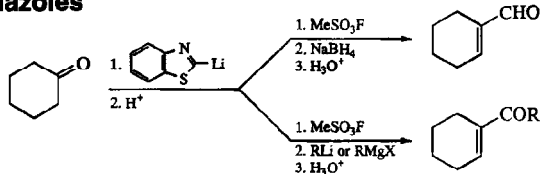
JOC 40 2021, 2025 (1975)

9. Thiazoles



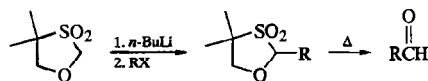
JOC 54 693 (1989); 55 1439 (1990); 58 275 (1993); 59 3656 (1994); 60 4749, 7927, 8074 (1995)
 TL 34 619 (1993)

10. Benzothiazoles



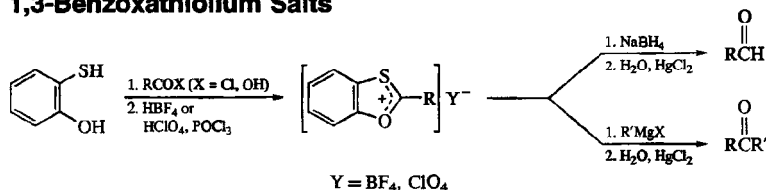
TL 5 (1978)

11. 1,3-Oxathiolane-3,3-dioxides



TL 3375 (1979)

12. 1,3-Benzoxathiolium Salts



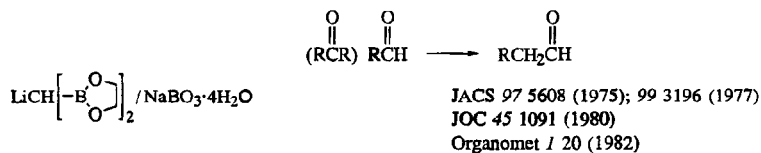
J Heterocyclic Chem 11 507, 943 (1974)

Gazz Chim Ital 105 907 (1975)

JCS Perkin I 323 (1976)

12. CARBONYL HOMOLOGATION

See also page 327, Section 4; page 1275, Section 4; page 1287, Section 8; page 1435, Section 9;
page 1441, Section 6; page 1451, Section 10; page 1461, Section 11; page 1475, Section 13;
and page 1513, Section 13.



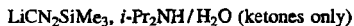
TL 28 1847 (1987)



Organomet 1 553 (1982)

JACS 107 5391 (1985); 113 5883 (1991)

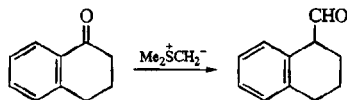
JOC 55 2369 (1990)



SL 109 (1994)

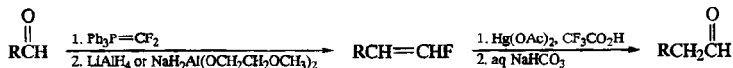


JACS 99 4536 (1977)

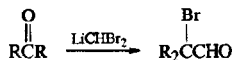


J Nat Prod 44 557 (1981)

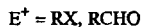
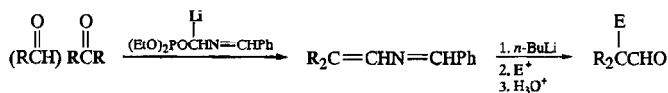
Syn Commun 12 613 (1982)



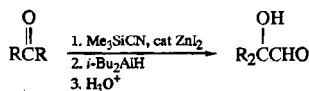
CL 651 (1980)



JOC 58 5493 (1993)

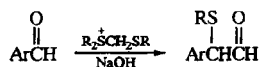


See page 1507, Section 11.

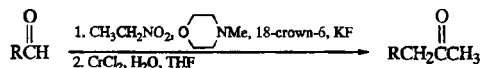


JACS 107 4577 (1985)

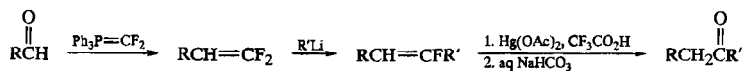
SL 479 (1991)



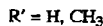
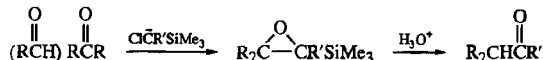
TL 35 6141 (1994)



JOC 59 1967 (1994)



CL 935 (1980)



CC 513 (1977)

JACS 99 4536 (1977)

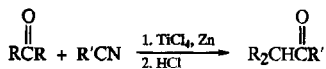
Organomet 1 893 (1982)

Tetr 39 867 (1983)

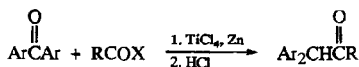


CC 774 (1981)

JOC 58 3687 (1993)



TL 34 1617 (1993)

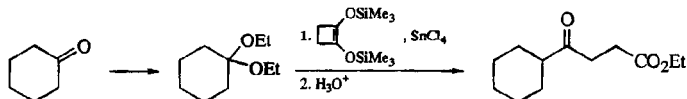


X = Cl, OR

TL 34 2963 (1993)

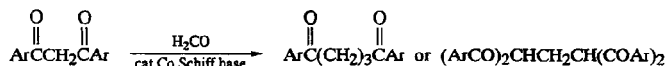


TL 35 6897 (1994)

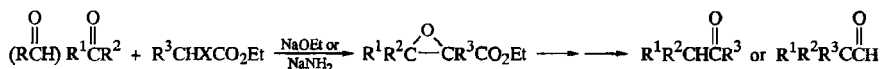


JOC 42 4166 (1977)

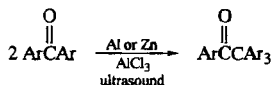
Org Syn Coll Vol 8 578 (1993)



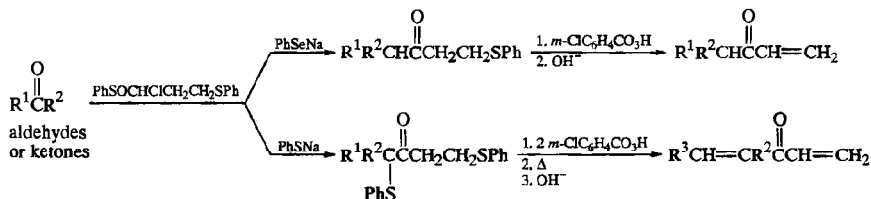
TL 36 5609 (1995)



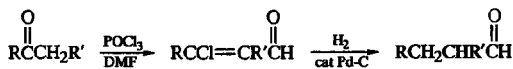
Org Rxns 5 413 (1949) (review)



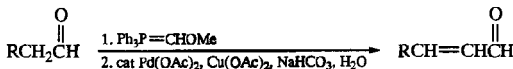
TL 31 4165 (1990)



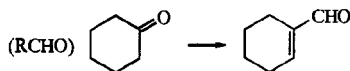
TL 27 2471 (1986)



Org Prep Proc Int 14 9 (1982)



JOC 57 2175 (1992)



PhSOCHClLi / KOH / Δ

TL 1377 (1977)

JOC 44 450 (1979)

PhSOCHClLi / LiClO₄, *n*-Bu₃PO, Δ

JACS 111 7504 (1989); 114 6910 (1992); 116 9027 (1994)

LiCHCl₂ / Δ / CaCO₃, LiClO₄, HMPA, Δ

TL 2465 (1973)

CC 1351 (1987)

CH₃NO₂, piperidine / TiCl₃

Syn 196 (1974)

TsNHNH₂ / *n*-BuLi / DMF

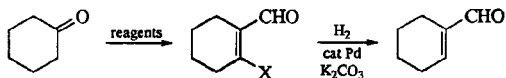
TL 2287 (1976)

Ph₃P=CHOMe / DDQ

TL 29 273 (1988)

LDA / (PhS)₂ / Ph₃P=CHOMe / HgCl₂, HCl

JOC 56 5224 (1991)



X

Reagents

Cl

COCl₂, DMF

Coll Czech Chem Commun 24 2385 (1959)

Ber 93 2743 (1960)

Proc Chem Soc 227 (1958)

POCl₃, DMF

Coll Czech Chem Commun 24 2385 (1959)

Ber 93 2743 (1960)

JOC 30 1126 (1965); 48 1921 (1983) (regio-selectivity); 51 2162 (1986)

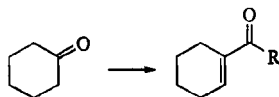
TL 31 5227 (1990); 32 643 (1991)

JACS 114 5018 (1992)

Br

PBr₃ or POBr₃, DMF

Coll Czech Chem Commun 26 3059 (1961)

RCHBrCO₂R', NaOEt / NaOH / Pb(OAc)₄

TL 1321 (1979)

Tf₂O, base / *n*-BuOCH=CH₂, cat Pd(OAc)₂, Et₃N / HCl (R = Me)

JOC 54 1502 (1989)

$\text{Me}_3\text{SiC}\equiv\text{CCeCl}_2/\text{HCO}_2\text{H}$ ($\text{R} = \text{Me}$)

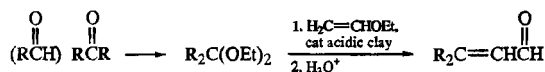
JOC 59 6922 (1994)

TsCH_2NC , POCl_3/RX , $\text{KO}-t\text{-Bu}/\text{H}^+$

JOC 60 2188 (1995)



TL 22 2021 (1981)



Syn 137 (1981)



$\text{LiCH}=\text{CHOEt}/\text{H}_2\text{O}$

JOC 57 7143 (1992)

$(\text{EtO})_2\text{POCH}(\text{Na})\text{CH}=\text{NCy}/\text{H}_3\text{O}^+$

Org Syn Coll Vol 6 358 (1988)

$\text{Ph}_3\text{P}=\text{CHCH}=\text{NNMe}_2/\text{hydrolysis}$

TL 31 341 (1990)

$\text{Et}_3\text{SiCH}_2\text{CH}=\text{N}-t\text{-Bu}/\text{sec-BuLi}$ or $\text{LDA}/\text{H}_3\text{O}^+$

JOC 59 5496 (1994)

JACS 117 8258 (1995)

$(\text{Me}_3\text{Si})_2\text{CHCH}=\text{N}-t\text{-Bu}$, cat $\text{ZnBr}_2/\text{H}_2\text{O}$, cat ZnCl_2

TL 31 349 (1990)

JOC 58 2517 (1993)

$\text{Me}_3\text{SiCH}_2\text{CH}=\text{N}-t\text{-Bu}$, cat $\text{CsF}/\text{H}_3\text{O}^+$

JOC 60 6582 (1995)

$(\text{Me}_3\text{Si})_2\text{CHCH}=\text{N}-t\text{-Bu}/\text{cat } n\text{-Bu}_4\text{NF}$

TL 31 349 (1990)

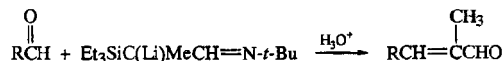
$n\text{-Bu}_3\text{SnCH}=\text{CHOEt}$, $\text{BF}_3\cdot\text{OEt}_2/\text{H}_2\text{O}$, MeOH

TL 36 5127 (1995)

$\text{Cp}_2\text{ZrClCH}=\text{CHOEt}$, cat $\text{AgClO}_4/\text{H}_3\text{O}^+$

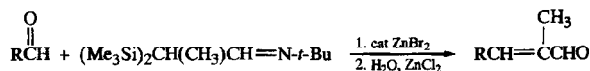
TL 34 341 (1993)

See also page 327, Section 4.

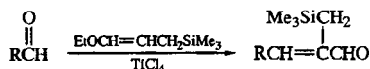


TL 26 2391 (1985)

JOC 60 7230 (1995)



JOC 58 2517 (1993)

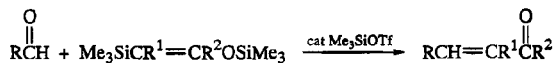


TL 29 4717 (1988)



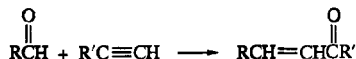
$\text{Me}_3\text{SiCH}_2\text{C}(\text{Me})=\text{N}-t\text{-Bu}$, cat $\text{CsF}/\text{H}_3\text{O}^+$ JOC 60 6582 (1995)

$(\text{Me}_3\text{Si})_2\text{CHC}(\text{Me})=\text{N}-t\text{-Bu}$, cat $\text{ZnBr}_2/\text{H}_2\text{O}$, ZnCl_2 JOC 58 2517 (1993)



R^1 or $\text{R}^2 = \text{H}$

TL 34 7745 (1993)

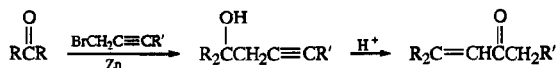


AlCl_3

TL 36 7277 (1995)

SbF_5

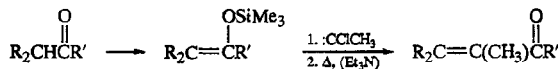
SL 195 (1995)



Syn Commun 10 637 (1980)



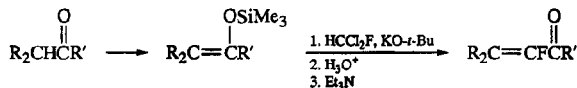
JOC 59 4725 (1994)



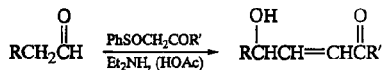
$\text{R}' = \text{H}$ or alkyl

Syn 289, 291 (1981)

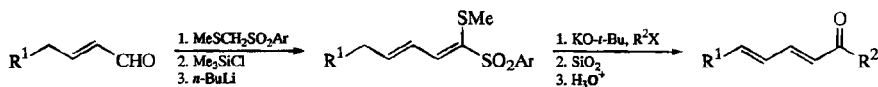
TL 22 645 (1981)



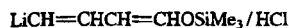
BSCF 455 (1985)



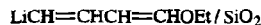
TL 28 649 (1987)



TL 31 4621 (1990)



Syn Commun 20 2983 (1990)



TL 717 (1978)

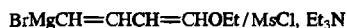
JACS 110 470 (1988)



JCS 4082 (1956)

JOC 47 4611 (1982)

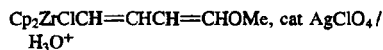
TL 31 3363 (1990)



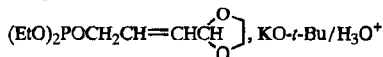
JACS 116 1753, 2621 (1994)



TL 34 5281 (1993)



TL 34 341 (1993)



TL 31 3129 (1990)



Acta Chem Scand B 42 569 (1988)

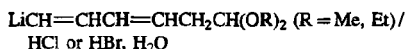
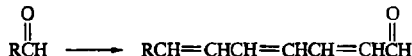
JOC 55 5313 (1990)



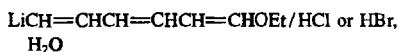
TL 27 4583 (1986)



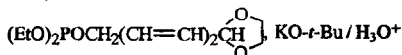
TL 32 4495, 4499 (1991)



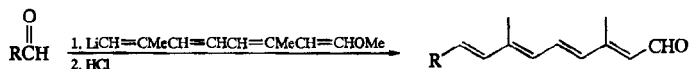
TL 30 7377 (1989)



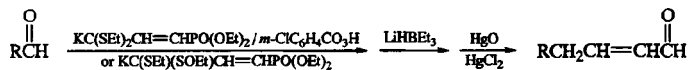
TL 30 7377 (1989); 34 7399 (1993)



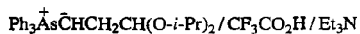
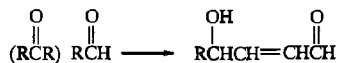
TL 31 3129 (1990)



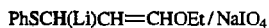
TL 34 319 (1993)



Can J Chem 58 2780 (1980)



TL 30 179 (1989)



JOC 54 2779 (1989)

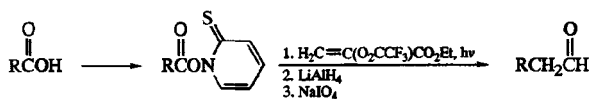


JACS 93 1724 (1971)

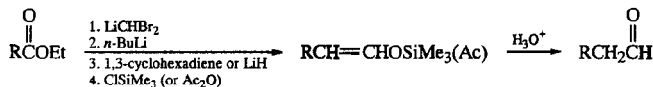
Org Syn Coll Vol 6 683 (1988)



JOC 47 1618 (1982)



TL 34 6505 (1993)



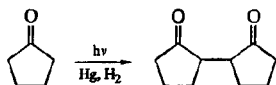
JACS 108 1325 (1986)

TL 28 2463 (1987)

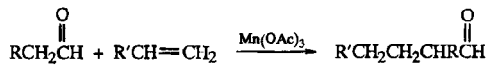
13. ALKYLATION AND ACYLATION OF ALDEHYDES, KETONES AND THEIR DERIVATIVES

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.1, p 1

1. Free Radical Alkylation



JACS 113 2233 (1991)



JOC USSR 8 1422 (1972)



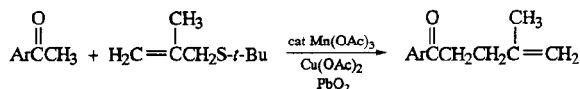
PbO ₂	Syn 315 (1976)
MnO ₂	Syn 315 (1976)
Co peroxide	Syn 315 (1976)
Ni peroxide	Syn 315 (1976)
Cu ₂ O	Syn 315 (1976)
CuO	Syn 315 (1976)
Ag ₂ O	Coll Czech Chem Commun 41 746 (1976)
AgO	Coll Czech Chem Commun 41 746 (1976)

cat AgNO₃, cat Na₂S₂O₈

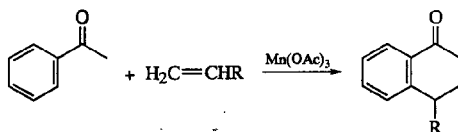
J Chem Res (S) 310 (1983)

HgO

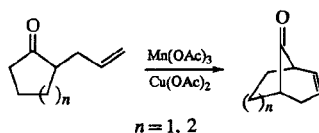
Syn 315 (1976)



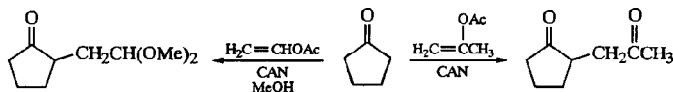
TL 31 357 (1990)



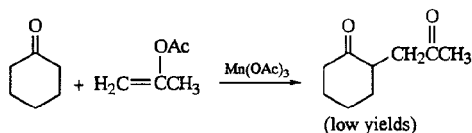
JACS 94 2888 (1972)



JOC 60 5376 (1995)



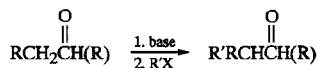
See page 1485, Section 4.2.



See page 1485, Section 4.2.

2. Direct Enol or Enolate Alkylation and Acylation

For aldol and related reactions, see page 1317, Section 8.



Reviews and key references:


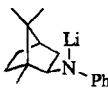
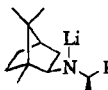
Rec Chem Prog 24 43 (1963) (general); 28 99 (1967) (general)

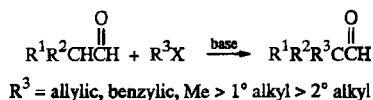
H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Menlo Park, California, 2nd ed (1972), pp 546-70 (general)

Tetr 32 2979 (1976) (regiospecific preparation of ketone enolates and synthetic uses); 33 2737 (1977) (structure and reactivity of alkali metal enolates)

- Ber 114 2866 (1981) (substituent effects on O vs C alkylation)
 JOC 48 4789 (1983) (stereochemistry and O vs C alkylation)
 D. A. Evans in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984),
 Vol 3, Chpt 1 (stereoselective alkylation reactions of chiral metal enolates)
 SL 173 (1991) (chiral lithium amide bases)
 Tetr Asym 2 1 (1991) (chiral lithium amide bases)
 TL 35 3065, 3069 (1994) (Mn enolate monoalkylation)

Bases for kinetic enolate formation

- LiCPh₃** JOC 30 1341 (1965); 34 3070 (1969); 37 3873 (1972)
 JCS Perkin I 2306 (1981)
- LiN(*i*-Pr)₂** JOC 34 2324 (1969); 36 2361 (1971); 39 3459 (1974)
 Org Syn 52 39 (1972)
 TL 22 4119 (1981); 29 3351 (1988); 30 2779 (1989); 31 4569 (1990); 33 8005 (1992)
 JACS 99 247 (1977); 101 934 (1979); 113 3123 (1991)
 JCS Perkin I 2306 (1981)
 Tetr 37 3981 (1981)
 Org Syn Coll Vol 6 121 (1988)
- LiN(*i*-Pr)(*c*-C₆H₁₁)** TL 965 (1973)
- LiTMP** TL 22 4119 (1981)
 JACS 113 3123, 9571 (1991)
- LiNRCHPhMe** JOC 57 3599 (1992)
- LiN(*i*-Pr)CHArCH₂X (X = H, OMe, NR₂)** JACS 108 543 (1986)
 (enantioselective) TL 36 5465 (1995)
- MeOCH₂CH₂OCH₂CH₂N(Li)CHPhCH₂N**  CC 1657 (1990)
 (enantioselective)
- LiN(CHPhCH₃)₂** (enantioselective) JOC 45 755 (1980); 57 3599 (1992)
 TL 23 105 (1982); 27 631, 2767 (1986); 36 5465 (1995)
-  (enantioselective) CC 88 (1986)
 JOC 57 3599 (1992)
-  (enantioselective) CC 88 (1986)
 TL 28 3723 (1987)
- LiN[Si(CH₃)₃]₂** JOMC 1 476 (1964)
 CC 1497, 1498 (1969)
 JACS 113 3123 (1991)
- LiN(SiMe₂Ph)₂** JACS 104 5526 (1982)
 JOC 52 4681 (1987); 58 5878 (1993)
- NaN[Si(CH₃)₃]₂** TL 30 2779 (1989)
- ClMnNRR'** TL 35 3065 (1994) (monoalkylation)

BaseNaOH, *n*-Bu₄NI

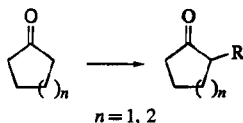
TL 1273 (1973)
Chem Ind 731 (1978)
Ann 1585 (1979)

KH

TL 491 (1978); 21 4005 (1980)
JOC 47 2479 (1982) ($R^1 = SPh$)

KCPb₃

JOC 50 2668, 2676 (1985)

LiN(SiMe₃)₂/MnBr₂/MeI

TL 34 7395 (1993)

K-Al₂O₃, hexane/*n*-BuBr

JOMC 204 281 (1981)

KH, Et₂O/ROTF

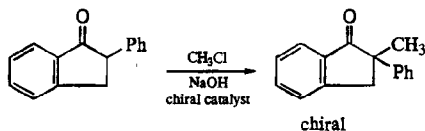
JOC 58 4469 (1993)

KO-*t*-Am, DME/RX ($R = \text{Me, PhCH}_2$)

Syn Commun 8 563 (1978)

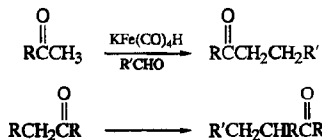
PhMnCl, cat PhNHMe/RX

SL 191 (1995)



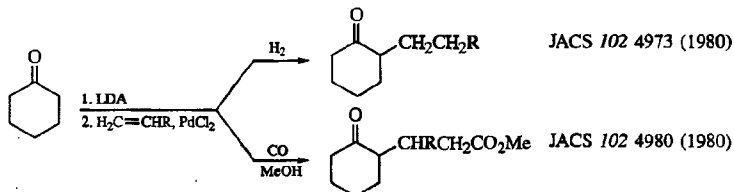
JACS 106 446 (1987)

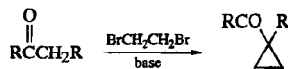
JOC 52 4745 (1987)



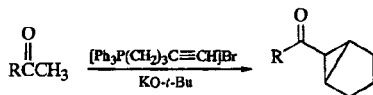
TL 2491 (1973)

JCS Perkin I 1273 (1975)

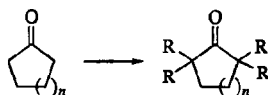




JOC 55 5454 (1990)



TL 35 335 (1994)


 NaH, Me₂SO₄ or EtI

Ber 122 1791 (1989)

KH, MeI

JOC 43 1834 (1978); 55 5454 (1990)

KOH, MeI, DMSO

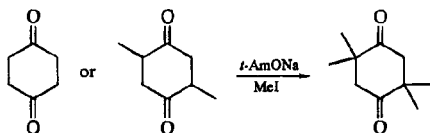
TL 31 859 (1990)

KOH, MeI, cat 18-crown-6

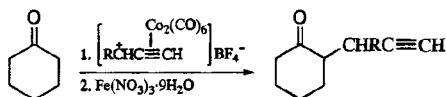
Ann 263 (1987)

 KO-*i*-Bu, MeI

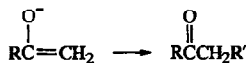
JOC 59 8299 (1994)



TL 24 2104 (1983)



JACS 102 2508 (1980)


R'
Reagent(s)

 CH₃

 CH₃I

CC 149 (1985) (stereochemistry)

 CH₃, CH₃CH₂

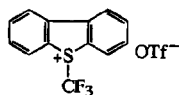
 CH₃I or CH₃CH₂I

BSCF II 318 (1982)

 CH₃, *n*-C₄H₉


 Me₂Zn, HMPA / R'I

JOC 54 1785 (1989)

 CF₃


JACS 115 2156 (1993)

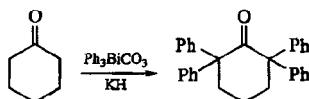


<u>R'</u>	<u>Reagent(s)</u>	
NO_2CMe_2	$\text{ClCMe}_2\text{NO}_2$	JACS 101 3378 (1979); 103 4610 (1981) JOC 47 1879 (1982)
	$(\pi\text{-C}_3\text{H}_5)\text{MCp}^+\text{X}/\text{I}_2$ (M, X = Rh, PF ₆ , Ir, OTf)	JACS 112 6420 (1990)
adamantyl	adamantyl iodide, hv	JOC 55 3705 (1990)
$\text{RCH}=\text{CHCH}_2$	$\text{RCH}=\text{CHCH}_2\text{OAc}$, cat. Pd(DBA) ₂	CC 1158 (1981)
$\text{CH}_3\text{OCH}_2\text{OC}(=\text{CH}_2)\text{CH}_2$	$\text{ClCH}_2\text{C}(=\text{CH}_2)\text{OCH}_2\text{OCH}_3$	JOC 55 3390 (1990)
$\text{H}_2\text{C}=\text{C}(\text{SO}_2\text{Ph})\text{CHR}$	$\text{RCH}=\text{C}(\text{SO}_2\text{Ph})\text{CH}_2\text{Br}$	TL 27 5095 (1986)
$\text{RCH}=\text{C}(\text{SO}_2\text{Ph})\text{CH}_2$	$\text{H}_2\text{C}=\text{C}(\text{SO}_2\text{Ph})\text{CHROAc}$	TL 27 5095 (1986)
Ph	Ph_3BiCO_3 $(\text{Ph}_2\text{I})\text{I}$	CC 246 (1980) JOC 60 2276 (1995)
<i>p</i> -NO ₂ C ₆ H ₄	<i>p</i> -(NO ₂) ₂ C ₆ H ₄ , KO- <i>t</i> -Bu, NH ₃ <i>p</i> -NO ₂ C ₆ H ₄ CHO, KO- <i>t</i> -Bu, NH ₃	CL 31 (1986) CL 173 (1986)
aryl	ArH, KO- <i>t</i> -Bu, NaNH ₂ or KNH ₂ ; NH ₃ ArX	Heterocycles 17 177 (1982) F. Terrier, "Nucleophilic Aromatic Displacement: The Influence of the Nitro Group," VCH, New York (1991) (review) "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Part 2.1, p 423 (review) JOC 57 5577 (1992)
	ArX, base	BSCF 302 (1971); 3493 (1973) Tetr 29 1843 (1973) JOC 40 2853 (1975)
	ArX, hv	JACS 94 683 (1972); 97 2507 (1975); 102 7765 (1980); 107 2183 (1985) (purines); 116 8169 (1994) TL 4519 (1973); 28 91 (1987) JOC 38 1407 (1973); 41 1702 (1976); 42 1481, 2481 (pyridines) (1977); 44 2604 (1979); 46 5022 (1981); 52 3880 (1987); 57 247 (1992)

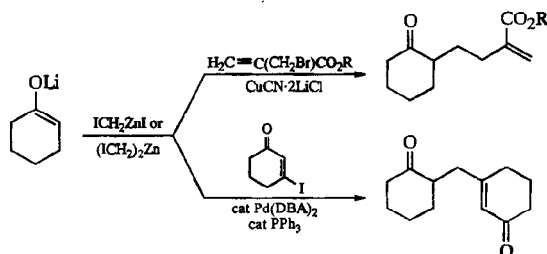
ArX, Ni(COD)₂

ArX, cat SmI₂

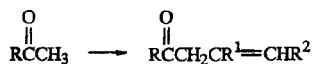
Acct Chem Res 11 413 (1978)
 Org Prep Proc Int 10 225 (1978)
 (review)
 Bull Soc Chim Belg 93 547
 (1984) (heterocycles)
 TL 4519 (1973)
 JACS 97 2507 (1975)
 TL 35 5185 (1994)



CC 246 (1980); 732 (1982)



JOC 58 2694 (1993)



base/ $\text{ICR}^1=\text{CHR}^2$, NH_3 , $h\nu$

JOC 41 1707 (1976)

RLi (on enol silane)/ ZnCl_2 / $\text{PhSeCH}_2\text{COR}^1$ / MsCl , Et_3N ($\text{R}^1 = \text{H}$ or Me , $\text{R}^2 = \text{H}$)

CC 434 (1981)

JOC 47 1632 (1982)

$\text{MeNHCH}_2\text{CH}_2\text{NMe}_2$ / n - BuLi / ZnCl_2 / $\text{ICH}=\text{CHR}^2$, cat $\text{Pd}(\text{PPh}_3)_4$

CL 1007 (1987)

LDA / $\text{PhSeCH}_2\text{CHO}$ / MsCl , Et_3N ($\text{R}^1 = \text{R}^2 = \text{H}$)

JACS 102 7950 (1980)

JOC 52 2760 (1987)

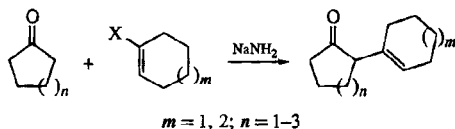
LDA / $\text{R}^2\text{CH}(\text{CHO})\text{SiMe}_2(t\text{-Bu})$ / $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{R}^1 = \text{H}$)

JACS 103 6251 (1981)

LDA / $[\text{R}^2\text{CH}=\text{C}(\text{OEt})\text{R}^1-\text{F}^+(\text{CO})_2\text{C}_5\text{H}_5]\text{BF}_4^-$ / HBF_4 / NaI ($\text{R}^1, \text{R}^2 = \text{H}$, H , H , Me , Me , H)

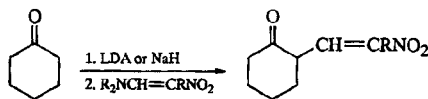
JACS 102 5930 (1980); 106 7264 (1984); 111 5252 (1989)

JOC 46 4103 (1981)

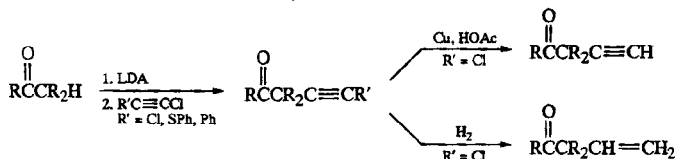


Tetr 28 4835 (1972); 30 1237 (1974)

TL 31 7603 (1990)

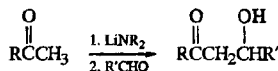


Syn 729 (1987)

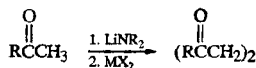


TL 23 2373 (1982)

JACS 106 3551 (1984)



See "Aldol and Related Reactions," page 1317, Section 8.

 MX_2 FeCl_2 CuCl_2 $\text{Cu}(\text{OTf})_2$

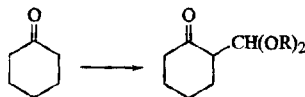
JOC 45 5408 (1980)

JACS 97 2912 (1975); 99 1487 (1977)

JOC 54 2190 (1989) (intramolecular)

TL 3741 (1977); 3555 (1978)

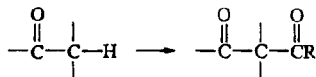
Chem Pharm Bull 28 262 (1980) (inter- and intramolecular)

 $[(\text{EtO})_2\text{CH}]\text{BF}_4, i\text{-Pr}_2\text{NEt}$ $\text{TiCl}_4, i\text{-Pr}_2\text{NEt} / \text{OMe}$

JOC 46 2557 (1981)

JACS 112 8215 (1990)

See also page 1494, Section 7.2.


 2,4,6-Me₃C₆H₂Li / RCOCl

TL 1187 (1977); 36 691 (1995)

Helv 64 716 (1981)

MeLi (on enol silane) / RCOCl

Helv 64 716 (1981)

 base / RCO₂R'

JACS 67 1510 (1945)

Org Rxns 8 59 (1954) (review)

LDA / RCOCl

JOC 55 3424 (1990)

 LDA / RCO₂CO₂Et

JOMC 127 C65 (1977)

 LiN(CHMePh)₂ / CF₃CO₂R

JOC 59 2748 (1994)

LDA / RCON(OMe)Me

JOC 54 4229 (1989)

LDA / RCOCN

TL 1339 (1979); 35 3653 (1994)

JACS 112 6965 (1990)

 LiN(SiMe₃)₂ / RCOPO(OEt)₂

CL 1087 (1981)

 RCOCl (on enamine) / H₃O⁺

JACS 76 2029 (1954); 85 207 (1963)

Ber 92 652 (1959); 93 913 (1960); 99 823 (1966)

 (RCO)₂O, BF₃

J Prakt Chem 141 149 (1934)

JACS 75 5030 (1953)

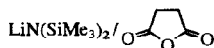
Org Rxns 8 59 (1954) (review)

Org Syn Coll Vol 3 16 (1955); 6 245 (1988)

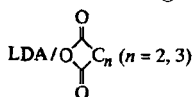
JOC 34 1425 (1969); 52 3986 (1987)

CC 85 (1979)

TL 23 1115 (1982)



TL 34 5189 (1993)



JOC 55 3424 (1990)

 KH / R₂C=C=O

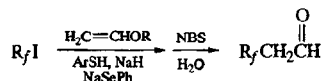
JOC 55 3634 (1990)



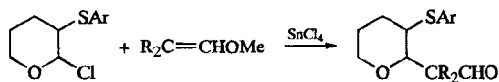
TL 30 1253 (1989)

3. Enol Ethers

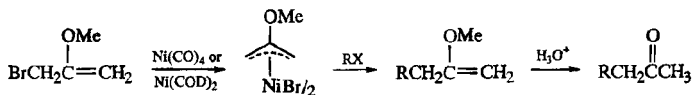
See also page 1441, Section 6.



TL 32 3385 (1991)

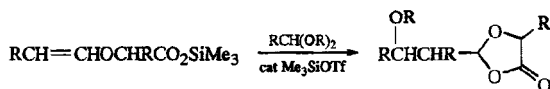


TL 34 3047 (1993)

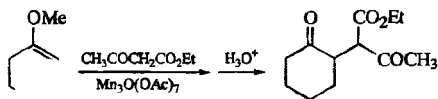


R = 1°, 2° alkyl; allylic; benzylic; aryl; vinylic

JACS 96 3250 (1974)



JACS 113 3418 (1991)

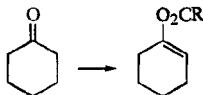


TL 28 175 (1987)

4. Enol Esters

4.1. Synthesis of Enol Esters

See also page 1636, Section 5.



Review: JACS 102 1966 (1980)

Ac₂O, NaOAc

Ber 42 1161, 2014 (1909)

Ac₂O, KOAcJACS 66 1325 (1944); 74 5381 (1952)
BCSJ 59 751 (1986)Ac₂O, K₂CO₃

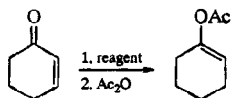
JOC 48 2705 (1983)

Ac₂O, Et₃N, cat DMAP

Syn Commun 9 157 (1979)

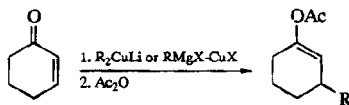
Ac₂O, cat TsOHJACS 67 1430 (1945)
JOC 26 3729 (1961); 28 3362 (1963); 32 1741
(1967); 48 1921 (1983) (regioselectivity)
JCS 2933 (1965)

Ac ₂ O, cat HClO ₄	JOC 30 2502 (1965); 32 1741 (1967); 33 943 (1968); 36 2361 (1971) Tetr 23 4143 (1967) Org Syn 52 39 (1972)
(PhCO) ₂ O, cat HClO ₄	JOC 34 1962 (1969)
H ₂ C=C(Me)OAc, cat TsOH	Ind Eng Chem 41 2920 (1949) JOC 28 3362 (1963); 30 1341, 2502 (1965); 33 935 (1968); 36 2361 (1971); 48 1921 (1983) (regio- selectivity)
H ₂ C=C(Me)OAc, cat TsOH, Cu(OAc) ₂	BCSJ 59 751 (1986)
H ₂ C=C(Me)OAc, Amberlyst 15	Ind J Chem B 21 358 (1982)
LiN(SiMe ₃) ₂ / Ac ₂ O	JOC 47 5088 (1982)
LiN(SiMe ₃) ₂ / ClCO ₂ R	TL 36 4795 (1995)
KH / AcCl, (DMAP)	Syn 504 (1979)
PhRNMnX (R = Me, <i>n</i> -Bu; X = Cl, Me, Ph) / (RCO) ₂ O	TL 35 6295 (1994)

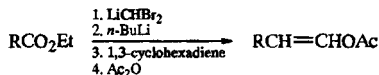


Reagent

LiHB(<i>sec</i> -Bu) ₃	JOC 47 5088 (1982)
[CuH(PPh ₃) ₆]	JOC 59 6313 (1994)

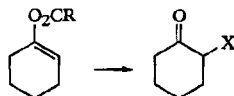


JOC 47 5088 (1982); 56 3344 (1991)

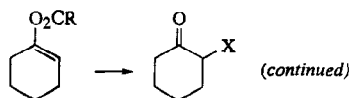


JACS 108 1325 (1986)

4.2. Applications

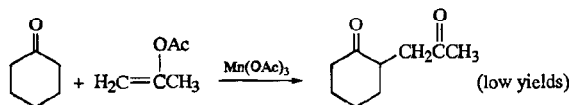


X	Reagent(s)	
H	MeLi / (CH ₃) ₂ CHCH ₂ CH(OH)CO ₂ Me (enantioselective)	TL 32 4729 (1991)

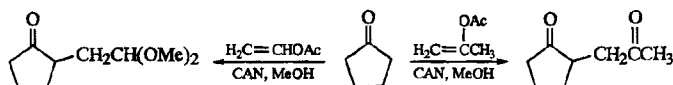


X	Reagent(s)	
	chiral ArOH (enantioselective)	JOC 60 1914 (1995)
	chiral R ₂ NH·HCl (enantioselective)	Tetr Asym 4 247 (1993)
	<i>Pichia farinosa</i> (enantioselective)	TL 33 6367 (1992)
	<i>Pichia miso</i> IAM 4682 (enantioselective)	JACS 112 9614 (1990)
R	MeLi/RX	JOC 30 2502 (1965); 32 1741 (1967); 33 935, 943 (1968); 36 2361 (1971); 51 2408, 2416 (1986)
	MeMgI/RX	Org Syn 52 39 (1972)
	CH ₂ I ₂ , Zn-Cu/RX	JACS 109 3147 (1987)
		Org Syn Coll Vol 6 121 (1988)
	MeMgI/RX	JCS 2933 (1965)
	CH ₂ I ₂ , Zn-Cu/RX	JACS 102 1966 (1980)
CH ₃	M ⁺ / CH ₂ I ₂ , Zn-Cu	JOC 34 1962 (1969)
CF ₃	Na, <i>t</i> -BuO ₂ H, cat Cu(OTf) ₂	TL 33 1291 (1992)
R _f	R _f I, AIBN/H ₃ O ⁺	TL 33 2489 (1992)
CH ₂ CH=CH ₂	H ₂ C=CHCH ₂ OCO ₂ Me, cat Pd ₂ (DBA) ₃ ·HCCl ₃ , cat dppe, cat <i>n</i> -Bu ₃ SnOMe	TL 24 4713 (1983)
CH ₂ C≡CR	Co ₂ (CO) ₈ CH ₂ C≡CR	See page 594, Section 8.
R ₂ C=CR	R ₂ C=CRBr, <i>n</i> -Bu ₃ SnOMe, cat PdCl ₂ (<i>o</i> -Tol ₃ P) ₂	BCSJ 57 242 (1984)
Ar	(ArN ₂)Cl, cat CuCl	BSCF 1926 (1972)
	ArX, <i>n</i> -Bu ₃ SnOMe, cat PdCl ₂ (<i>o</i> -Tol ₃ P) ₂	BCSJ 57 242 (1984)
		JACS 115 3499 (1993)
		TL 36 4315 (1995)
CHROH	MeLi/RCHO	JOC 56 3344 (1991)
	MeLi/ZnCl ₂ /RCHO	Org Syn Coll Vol 6 692 (1988)
COR	acylation or rearrangement Ac ₂ O, BF ₃ ·HOAc	JACS 102 1967 (1980) (review)
		Org Syn Coll Vol 6 245 (1988)
Br	Br ₂	See page 709, Section 1.

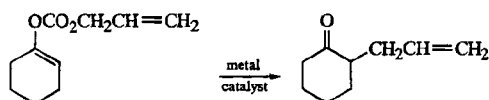
O_2CR	epoxidation electrolysis	JACS 102 1967 (1980) (review) JACS 97 6144 (1975)
$ArSO_3$	$(ArSO_3)_2$	Syn 760 (1985) TL 27 5811 (1986)



JOC 39 3457 (1974)



TL 28 5357 (1987)



Metal

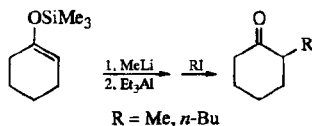
Mo, Rh, Ni

CL 1721 (1984)

Pd

TL 24 1793 (1983)

5. Enol Alanes



TL 1117 (1969)



E^+

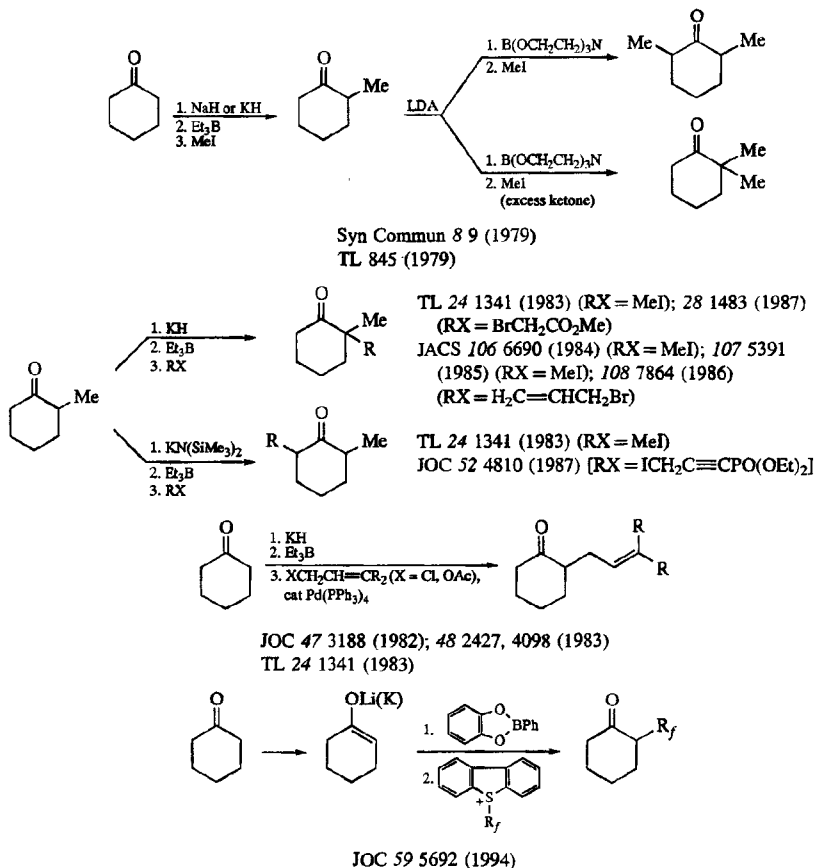
$RCH=CHCH_2Br$, $RCHO$, $RCOCl$

Ann 593 (1988)

Br_2

JOC 53 5534 (1988)

6. Enol Boranes



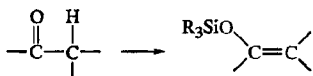
7. Enol Silanes

Reviews:

Syn 91 (1977); 1, 85 (1983)

Org Prep Proc Int 20 317 (1988)



7.1. Preparation




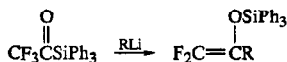
Thermodynamic enol silane

<i>t</i> -BuMe ₂ SiCl, imidazole, DMF	TL 34 6631 (1993)
Me ₃ SiCl, Et ₃ N, DMF	JOC 34 2324 (1969); 45 2307 (1980) TL 2671 (1978) Org Syn Coll Vol 8 460 (1993)
Me ₃ SiCl, NaI, Et ₃ N, CH ₃ CN	JOMC 201 C9 (1980) Org Syn 65 1 (1987) Org Syn Coll Vol 8 1 (1993)
Me ₃ SiCl, LiI, (Me ₃ Si) ₂ NH	JACS 107 268 (1985)
Me ₃ SiI, (Me ₃ Si) ₂ NH	Syn 730 (1979)
Me ₃ SiOTf, Et ₃ N	Syn 259 (1976); 1 (1982) (review) Ann 1643 (1981) Org Syn Coll Vol 8 286 (1993)
Et ₃ SiOTf, Et ₃ N	Ann 1643 (1981) Syn 1 (1982) (review)
Me ₃ SiOTf, DBU	Syn 206 (1985)
Na, anthracene / R ₃ SiCl (R = Me, Et)	BSCF 3552 (1967)
NaH / Me ₃ SiCl, Et ₃ N	JACS 90 4462 (1968)
KH / Et ₃ B / Me ₃ SiCl	TL 24 1341 (1983)
BrMgN(<i>i</i> -Pr) ₂ / Me ₃ SiCl	TL 24 1345 (1983)

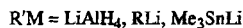
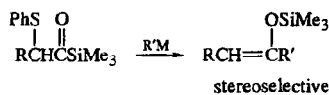
Kinetic enol silane

LiN(<i>i</i> -Pr) ₂ / Me ₃ SiCl	JOC 34 2324 (1969); 45 2307 (1980) JACS 113 3123, 5053 (1991) TL 33 8005 (1992)
LiN(<i>i</i> -Pr) ₂ / <i>t</i> -BuMe ₂ SiCl	JACS 98 2868 (1976) Helv 65 385 (1982) TL 34 6631 (1993)
LiN(<i>i</i> -Pr) ₂ or LiN(<i>t</i> -C ₄ H ₉)(<i>t</i> -C ₈ H ₁₇), Me ₃ SiCl, Et ₃ N	TL 25 495 (1984)
LiN(<i>i</i> -Pr)CHArCH ₂ X (X = H, OMe, NR ₂) / Me ₃ SiCl (enantioselective)	JACS 108 543 (1986) JOC 60 7837 (1995)
LiNRCHPhCH ₂ N  / Me ₃ SiCl (enantioselective)	JACS 114 761 (1992) TL 34 5105 (1993)
LiNRCHPhCH ₂ N  NMe / Me ₃ SiCl (enantioselective)	TL 30 6537, 7221 (1989); 33 8141 (1992); 34 5101 (1993) Heterocycles 30 307 (1990) JOC 57 5438 (1992); 60 7837 (1995)
various chiral LiNR ¹ R ² / Me ₃ SiCl (enantioselective)	TL 30 7241 (1989)

LiNRCHPhCH ₃ / Me ₃ SiCl (enantioselective)	TL 30 7221 (1989)
LiN(CHPhCH ₃) ₂ / Me ₃ SiCl (enantioselective)	TL 27 631 (1986) SL 321 (1991) JOC 58 533 (1993); 59 2748 (1994); 60 7837 (1995)
 Ph / Me ₃ SiCl (enantioselective)	CC 88 (1986) TL 28 3723 (1987)
LiTMP / Me ₃ SiCl	JACS 102 3959 (1980); 113 3123, 9571 (1991)
LiN(<i>t</i> -Bu)CMe ₂ CH ₂ CMe ₃ , Me ₃ SiCl	TL 25 495 (1984)
LiN(SiMe ₃) ₂ / Me ₃ SiCl	JOC 45 2307 (1980) JACS 113 3123 (1991)
LiN(SiMe ₃) ₂ / <i>t</i> -BuMe ₂ SiCl (enones)	CC 564 (1973)
KN(SiMe ₃) ₂ / Et ₃ B / Me ₃ SiCl	TL 24 1341 (1983)
LiN(SiPhMe ₂) ₂ / Me ₃ SiCl	JACS 104 5526 (1982); 108 3435, 3841 (1986)
(Me ₃ Si) ₂ NH, imidazole (β-diketones)	Syn 722 (1976)
PhRNMgX (X = Ph, Cl, OEt, NRPh)	TL 35 6295 (1994)
cat <i>n</i> -Bu ₄ NF, Me ₃ SiCH ₂ CO ₂ Et	JACS 98 2346 (1976); 108 3435, 3841 (1986) TL 2079 (1978) Org Syn Coll Vol 7 512 (1990)
cat <i>n</i> -Bu ₄ NF, CH ₃ CH=C(OMe)OSiMe ₃	Syn 1089 (1982)
Unknown or mixed regiochemistry	
Me ₃ SiCl, <i>n</i> -C ₄ H ₉ SO ₃ K, Et ₃ N	Syn 34 (1979)
Me ₃ SiCl, ZnCl ₂ , Et ₃ N	JACS 96 7807 (1974)
Me ₃ SiO ₃ SF, Et ₃ N	TL 34 995 (1993); 35 5285 (1994)
<i>t</i> -BuMe ₂ SiOTf, Et ₃ N	TL 25 5953 (1984); 35 5285 (1994) JACS 109 7575 (1987)
<i>t</i> -BuMe ₂ SiOTf, 2,6-lutidine	TL 25 5953 (1984)
<i>i</i> -Pr ₃ SiOTf, Et ₃ N	TL 22 3455 (1981)
Me ₃ SiNMe ₂	TL 3553 (1974)
KH / Me ₃ SiCl, cat Et ₃ N, DME	Syn 504 (1979)

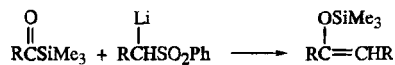


TL 33 1221 (1992)

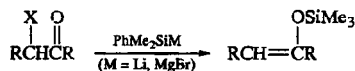


JOC 52 513 (1987)

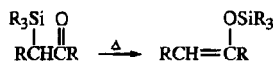
JACS 112 5609 (1990)



JACS 112 5609 (1990)

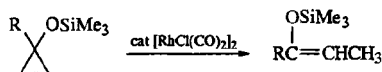


JACS 112 5609 (1990)

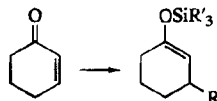


TL 30 283 (1989)

SL 199 (1993)

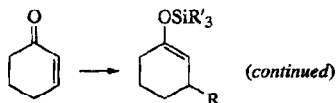


TL 30 6887 (1989)

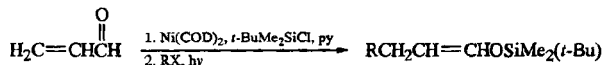


R Reagents

Li, NH ₃ , <i>t</i> -BuOH / Me ₃ SiCl	JACS 96 6181 (1974); 107 1440 (1985)
LiHB(<i>sec</i> -Bu) ₃ / Me ₃ SiCl	JACS 107 1440 (1985)
	JOC 52 1870 (1987)
<i>i</i> -Bu ₂ AlH, cat MeCu, HMPA / Me ₃ SiCl	JOC 52 439 (1987)
LiAlH ₄ , R ₃ SiOTf	SL 163 (1995)
R ₃ SiH, cat Co ₂ (CO) ₈	Organomet 10 2606 (1991)
R ₃ SiH, cat Co ₂ Rh ₂ (CO) ₁₂	Organomet 10 2606 (1991)
R ₃ SiH, cat Rh ₄ (CO) ₁₂	Organomet 10 2606 (1991)
R ₃ SiH, cat HRh(PPh ₃) ₄	TL 34 3095 (1993)
R ₃ SiH, cat ClRh(PPh ₃) ₃	TL 5035 (1972)
	Tetr 37 4515 (1981)
	Organomet 1 1390 (1982); 10 2606 (1991)
	JACS 111 6257 (1989)

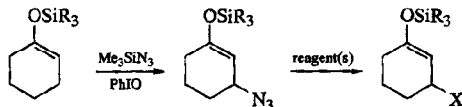
RReagents

	Et ₃ SiH, EtMe ₂ SiH or MePh ₂ SiH; cat [Pt(μ-H)(SiR ₃)PR ₃] ₂	JOMC 191 39 (1980)
	R ₃ SiH, cat Pt[H ₂ C=CHSiMe ₂ O-SiMe ₂ CH=CH ₂] ₂	JOC 59 2287 (1994)
	[HCu(PPh ₃) ₆]/Me ₃ SiCl	JACS 110 291 (1988) TL 30 5677 (1989); 31 3237 (1990) (both enals)
	PhSiMe ₂ Li / cat NaH	TL 31 831 (1990)
alkyl, aryl	RMgBr, cat CuBr·SMe ₂ , Me ₃ SiCl, HMPA (enals and enones)	TL 27 4025 (1986)
	RCu, Me ₃ SiCl, HMPA or DMAP (enals and enones)	TL 27 4029 (1986)
	RCu, Me ₃ SiCl, TMEDA	TL 28 27 (1987)
	RCu, Me ₃ SiH	JOC 58 7238 (1993)
	R ₂ CuLi / Me ₃ SiCl	JACS 96 6179 (1974) Tetr 37 4027 (1981)
	R ₂ CuLi / Ph ₂ SiMeCl	JOC 52 165 (1987)
	R ₂ CuLi, Me ₃ SiCl, HMPA or DMAP (enals and enones)	TL 27 4029 (1986)
	R ₂ CuLi, Me ₃ SiCl	TL 26 6015, 6019 (1985); 27 1047 (1986); 28 1973 (1987); 30 7087 (1989)
	MeCu(CN)Li, Me ₃ SiCl	TL 26 6019 (1985)
	MeCu(CN)Li, <i>t</i> -BuMe ₂ SiCl	TL 28 3589 (1987)
	R ₂ CuMgX / Me ₃ SiCl (enals)	JOMC 228 321 (1982)
vinyllic, acyl	<i>n</i> -Bu ₃ SnR, <i>t</i> -BuMe ₂ SiCl, cat Ni(COD) ₂	JACS 114 5160 (1992)



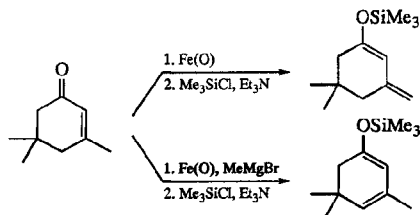
R = 1°, 2° alkyl; aryl; vinyllic; acyl

JACS 113 6172 (1991)

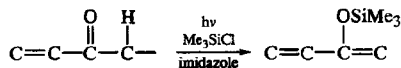


Reagents: ArH, Me₃Al or Me₂AlCl (X = Ar); Et₂AlCN (X = CN); *n*-Bu₃SnCH₂CH=CH₂, Me₂AlCl (X = CH₂CH=CH₂); RC≡CLi, Me₂AlCl (X = RC≡C); enol silane, Me₂AlCl (X = ketone); RCH=CHZrCl (X = RCH=CH)

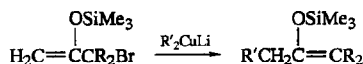
JACS 114 3993 (1992)



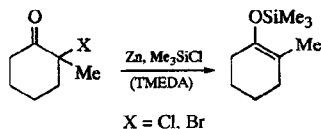
JACS 106 7619 (1984)



JOC 51 3335 (1986)

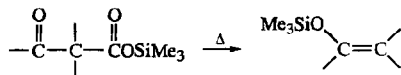


TL 21 2325 (1980)

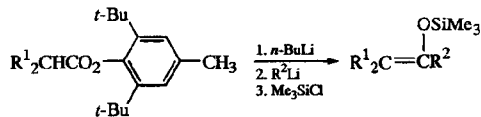


Syn Commun 7 327 (1977)

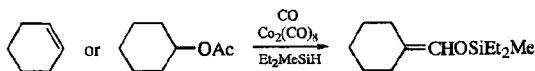
TL 24 507 (1983)



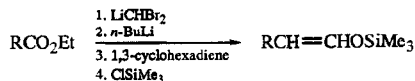
JACS 97 1619 (1975)



JACS 107 5396 (1985)



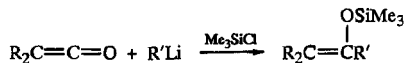
JACS 108 7361 (1986)



JACS 108 1325 (1986)

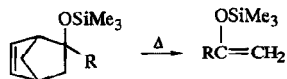


TL 29 1065 (1988)

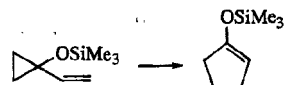


IACS 107 5391 (1985); 112 6396 (1990)

IOC 50 2105 (1985)



BSCF 1122 (1976)

 Δ

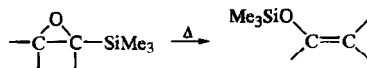
IACS 95 5311 (1973)

cat $\text{NiCl}_2(\text{PPh}_3)_2\text{-Zn}$

SL 941 (1994)

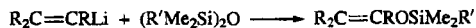


IACS 107 4260 (1985)



JOMC 94 C21 (1975)

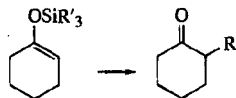
TL 1449, 1453 (1976)

 $\text{R}' = \text{Me}, t\text{-Bu}$

TL 29 4269 (1988)

7.2. Reactions

See also page 1546, Section 23.

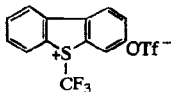


Reviews:

Chimia 265 (1980)

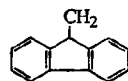
Pure Appl Chem 55 1749 (1983) (aldol review); 66 1487 (1994) (enantioselective alkylation)

Org Prep Proc Int 20 317 (1988)

<u>R</u>	<u>Reagents</u>	
H	MeLi, LiBr/chiral HNR ₂ chiral binaphthol-SnCl ₄ chiral imide	Tetr Asym 4 35 (1993) (chiral) JACS 116 11179 (1994) (chiral) Angew Int 33 107 (1994) (chiral)
CH ₃	CH ₂ I ₂ , Zn(Ag)/OH ⁻	TL 2767 (1973); 3327, 3333 (1974) JOC 39 858 (1974)
	MeLi, LiBr/chiral HNR ₂ /MeI MeLi/MnBr ₂ /MeI	Tetr Asym 4 35 (1993) (chiral) TL 34 7395 (1993)
CH ₃ , allylic	RX, AgO ₂ CCF ₃	TL 35 367 (1994)
CH ₃ , CH ₂ Ph	MeLi, LiBr/chiral HNR ₂ /RX	TL 34 1963 (1993) (chiral)
CF ₃		TL 31 3579 (1990) JACS 115 2156 (1993)
1° alkyl	ROTF, MABR RI, AgO ₂ CCF ₃	JACS 114 4422 (1992) TL 33 1855 (1992)
1° alkyl	RX, <i>n</i> -Bu ₄ NF, molecular sieves	JACS 117 5245 (1995)
1°, 2° alkyl	MeLi/ <i>n</i> -Bu ₃ SnCl/RX	TL 1117 (1969)
1°, 2° alkyl; allylic; benzylic	MeLi/RX	JACS 90 4464 (1968); 97 1619 (1975); 101 934 (1979) TL 1117 (1969) JOC 36 2361 (1971); 51 2408 (1986); 52 165 (1987); 58 3681 (1993)
1° alkyl, allylic	LiNH ₂ , NH ₃ /RX MeLi/R' ₃ Al/RX	JOC 39 2506 (1974); 40 2156 (1975) TL 1117 (1969); 31 4761 (1990)
1° alkyl, benzylic	RX, (PhCH ₂ NMe ₃)F	JACS 97 3257 (1975); 104 1025 (1982); 109 1269 (1987); 111 2302 (1989) JOC 52 3745 (1987)
1° alkyl, benzylic, allylic	RX, [(R' ₂ N) ₃ S]Me ₃ SiF ₂ (R' = Et, <i>i</i> -Pr)	TL 21 2085 (1980) JACS 102 1223 (1980); 105 1598 (1983); 115 3056 (1993)
2°, 3° alkyl; allylic, benzylic; CHRSR; CHROR; CH ₂ NMeCO ₂ Me	RX; SnCl ₄ , TiCl ₄ , ZnCl ₂ , ZnI ₂ or FeCl ₃	TL 4183 (1977); 1455, 4925 (1978); 995, 1427, 1519, 2179, 4971 (1979); 21 2010, 2033 (1980); 22 1101, 2321 (1981); 23 2399, 2601 (1982); 24 323, 327, 419, 2095 (1983); 29 1461 (1988); 30 5825 (1989); 33 7727 (1992)

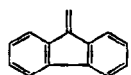
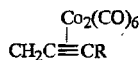
R

Reagents

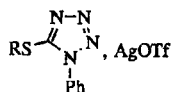
CH₂PhCHAr₂

CHRAr

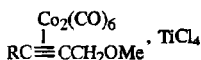
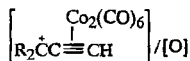
benzylic, allylic

benzylic, allylic, α-halo ester
allylicCR₂C≡CH, *n*-Bu₄NFMeLi, LiBr/chiral HNR₂/
PhCH₂Br(Ar₂CH)OTf

ArCHROCOCl, AgOTf

RX, (*n*-Bu₄N)Ph₃SnF₂allylic alcohol or acetate,
LiClO₄

allylic acetate, Lewis acid

H₂C=CHCH₂OAc or
H₂C=C(Me)CH₂OCO₂Me,
cat Pd₂(DBA)₃·HCCl₃, dppe*n*-BuLi/(R₂C=CHCH₂NEt₃)Br,
cat Pd(PPh₃)₄allylic nitro compound, SnCl₄
PhIO·HBF₄/alkeneAngew Int 17 48 (1978); 18 72
(1979); 21 96 (1982) (review)

BCSJ 52 1241 (1979)

JACS 101 984 (1979); 106 7630
(1984)

Ber 113 3734, 3741 (1980)

Syn 941 (1980); 1003 (1981)

JOC 45 3559 (1980); 47 3219

(1982); 53 611 (1988); 57

7143 (1992); 59 500 (1994);

60 1221 (1995)

Syn Commun 11 217 (1981)

Tetr 37 319, 4027 (1981)

JCS Perkin I 1099 (1982)

BSCF II 375 (1982)

Org Syn Coll Vol 7 424 (1990)

TL 36 2403 (1995)

JACS 116 8829 (1994) (chiral)

TL 34 3393 (1993)

TL 33 951 (1992)

TL 31 265 (1990)

TL 32 7381 (1991)

JOC 57 2986 (1992)

CC 1180 (1981)

JCS Perkin I 2079 (1982)

CL 1325 (1983)

TL 28 2397 (1987); 34 6627
(1993)Acct Chem Res 20 140 (1987)
(review)

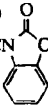
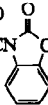
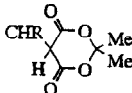
JOMC 236 409 (1982)




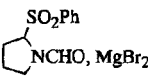


CC 1285 (1986)




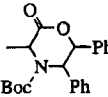
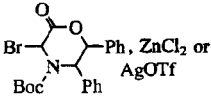




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

See page 594, Section 8.





JACS 114 2544 (1992)
(intramolecular)

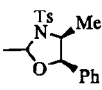
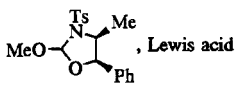

Ar	ArX ($\text{X} = \text{Br}, \text{I}$), $n\text{-Bu}_3\text{SnF}$, cat $\text{PdCl}_2(\text{PAr}_3)_2$ $(\text{Ph}_3\text{I})\text{F}$	JACS 104 6831 (1982) JOC 56 5764 (1991)
ArNO_2	$\text{NO}_2\text{-Ar-H}$, $[(\text{Me}_2\text{N})_3\text{S}]\text{Me}_3\text{SiF}_2$ / Br_2 or DDQ	JACS 107 5473 (1985)
$\text{CH}_2\text{CH}_2\text{SAr}$	$\text{ClCH}_2\text{CH}_2\text{SAr}$, Lewis acid	TL 24 961 (1983)
$\text{C}-\text{C}-\text{XPh}$ ($\text{X} = \text{S}, \text{Se}$)	$\text{Cl}-\text{C}-\text{C}-\text{XPh}$, ZnBr_2	TL 24 5911 (1983)
$\text{CH}(\text{CHRSPh})\text{CH}=\text{CHR}$	$\text{PhSCHRCH}(\text{OAc})\text{CH}=\text{CHR}$, cat Me_3SiOTf	TL 32 4311 (1991)
$\text{CHRCH}_2\text{NO}_2$	$\text{RCH}=\text{CHNO}_2$, $\text{Cl}_2\text{Ti}(\text{O-}i\text{-Pr})_2$, (KF)	Helv 68 319 (1985) Can J Chem 65 836 (1987) JOC 55 1349 (1990)
$\text{CH}_2\text{CH}_2\text{COR}$	$\text{R}-\text{CH}(\text{OH})-\text{CH}_2\text{COR}$, $\text{Mn}(\text{O}_2\text{CR})_3$ ($\text{R} = 2\text{-py}$)	BCSJ 66 819 (1993)
$\text{CHRCH}_2\text{COR}'$	$\text{RCH}=\text{CHCOR}'$, Lewis acid	See page 1571, Section 2.
$\text{CHRCH}_2\text{CO}_2\text{H}$	$\text{RCH}=\text{CH}-\text{CH}(\text{O}-\text{R}')-\text{CH}_2\text{CO}_2\text{H}$, $(\text{CF}_3\text{CO})_2\text{O} / \text{H}_3\text{O}^+$	TL 31 7433 (1990); 33 1743 (1992)
$\text{CR}_2\text{CH}_2\text{CO}_2\text{R}$	$\text{R}_2\text{C}=\text{CHC}(\text{OR})_3$, cat $(\text{Ph}_3\text{C})\text{ClO}_4$	CL 1183 (1987)
$\text{CHRCH}_2\text{COSR}$	$\text{RCH}=\text{CHCOSR}$, cat $\text{SbCl}_5\text{-Sn}(\text{OTf})_2$	CL 91 (1988)
CHRCH_2CN 	$\text{RCH}=\text{CHCN}$  , EtAlCl_2	TL 34 2421 (1993)
$\text{CH}_2\text{CH}(\text{CO}_2\text{R})_2$	$\text{H}_2\text{C}=\text{C}(\text{CO}_2\text{R})_2$, SnCl_4	SL 472 (1991)
	$\text{RCH}=\text{CH}-\text{CH}(\text{O}-\text{Me})-\text{CH}_2\text{CO}_2\text{R}$ / HCl	TL 34 7437 (1993)
$\text{CH}_2\text{CH}=\text{CHCH}_2\text{ONO}_2$	$\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$, CAN	JOC 60 4954 (1995)
$\text{CHRCH}=\text{CHCOR}$	$\text{PhCH}_2\text{OCHRCH}=\text{CHCOR}$, $\text{BF}_3\cdot\text{OEt}_2$	TL 34 4497 (1993)
$\text{CHRCH}=\text{CHCO}_2\text{R}$	$\text{AcOCHRCH}=\text{CHCO}_2\text{R}$, $\text{BF}_3\cdot\text{OEt}_2$	TL 32 1141 (1991)

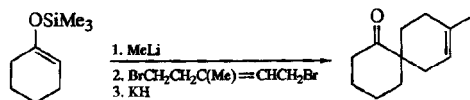
R	Reagents	
$\text{CH}_2\text{CH}=\text{CHSPh}$	$\text{PhSCH}_2\text{CH}=\text{CHSPh}$, SnCl_4	TL 33 5413 (1992)
$\text{CH}_2\text{CH}=\text{CRSPh}$	$\text{PhSCR}=\text{CHCH}_2\text{SnR}_3$, SnCl_4	TL 31 6685 (1990)
$\text{CH}_2\text{Cl}=\text{CHSO}_2\text{Ph}$	$\text{PhSO}_2\text{CH}=\text{ClCH}_2\text{I}$, AgBF_4	TL 32 5673 (1991)
CH_2CHO	$\text{H}_2\text{C}=\text{CHOEt}$, CAN , CaCO_3 / H_3O^+	SL 679 (1990)
CH_2COAr	$(\text{ArCOCH}_2\text{IPh})\text{BF}_4$	JOC 54 2605 (1989)
	$\text{PhIO}\cdot\text{HBF}_4$ / 	TL 29 3703 (1988)
$\text{CHR}^1\text{COCH}_2\text{R}^2$	$\text{R}^2\text{CH}_2\text{C}(\text{NO}_2)=\text{CHR}^1$, SnCl_4 / H_2O	JACS 98 4679 (1976); IO6 2149 (1984) Org Syn Coll Vol 7 414 (1990)
$\text{CH}_2\text{CO}_2\text{R}$	$\text{BrCH}_2\text{CO}_2\text{R}$, air, Et_3B	TL 35 2763 (1994)
$\text{CH}(\text{CF}_3)\text{CO}_2\text{Et}$	$\text{N}_2\text{C}(\text{CF}_3)\text{CO}_2\text{Et}$, cat $\text{Rh}_2(\text{OAc})_4$ / $n\text{-Bu}_4\text{NF}$ or HCl	JOC 55 3383 (1990)
CCl_2CF_3	CF_3CCl_3 , cat $\text{RuCl}_2(\text{PPh}_3)_3$	SL 403 (1990)
R_f	$\text{R}_f\text{I}(\text{Ph})\text{O}_3\text{SCF}_3$, py R_fI , cat Et_3B , 2,6-lutidine	TL 23 1471 (1982) TL 31 6391 (1990)
CH_2NHR	$(\text{MeOCH}_2\text{NR}=\text{CH}_2)\text{Cl}^-$	TL 31 4229 (1990)
CH_2NR_2	$\text{R}'\text{OCH}_2\text{NR}_2$, Me_3SiI or Me_3SiOTf $(\text{R}_2\text{N}=\text{CH}_2)\text{Cl}^-$ ($\text{R} = \text{Me}, \text{Et}$)	TL 23 547 (1982) CL 405 (1983) CC 269 (1986) TL 28 6355 (1987)
CHRNHR	$\text{RCH}=\text{NR}$, $\text{BF}_3\cdot\text{OEt}_2$	JOC 58 2302 (1993)
CHArNHar	$\text{ArCH}=\text{NAr}$, cat Me_3SiOTf	CC 1053 (1987)
$\text{CH}(\text{COPh})\text{NHPH}$	PhCOCHO , PhNH_2 , cat $\text{Yb}(\text{OTf})_3$, MgSO_4	TL 36 5773 (1995)
CHRNRCOR	MeOCHRNRCOR , $\text{BF}_3\cdot\text{OEt}_2$ ROCHRNRCOR , TiCl_4	JACS 103 1172 (1981) JOC 60 6114 (1995) TL 36 935 (1995) JACS 103 1172 (1981) JOC 57 5150 (1992)
	 NCHO , MgBr_2	SL 48 (1990)
	 , $(\text{MeO})_2\text{PS}_2\text{H}$, TiCl_4	SL 797 (1991)

	$\text{AcO}-\text{C}_4\text{H}_4\text{N}=\text{O}$, cat Me_3SiOTf	CC 1076 (1981) TL 28 507 (1987); 29 3129 (1988); 36 4563 (1995)
	$\text{AcO}-\text{C}_4\text{H}_4\text{N}=\text{O}$, ZnX_2 ($\text{X} = \text{Cl}, \text{Br}$)	TL 23 379, 2293 (1982) Can J Chem 62 2936 (1984) CL 1343 (1985) JACS 110 6879 (1988)
	$\text{MeO}-\text{C}_4\text{H}_4\text{N}=\text{O}$, $\text{BF}_3 \cdot \text{OEt}_2$	TL 35 6119 (1994)
$\text{CR}(\text{NHCOCH}_3)\text{CO}_2\text{Et}$	$\text{AcOCR}(\text{NHCOCH}_3)\text{CO}_2\text{Et}$, $\text{BF}_3 \cdot \text{OEt}_2$	JOC 58 3259 (1993)
$\text{CPh}(\text{NHCO}_2\text{Me})\text{CO}_2\text{Me}$	$\text{MeOCPh}(\text{NHCO}_2\text{Me})\text{CO}_2\text{Me}$, $\text{BF}_3 \cdot \text{OEt}_2$	JOC 58 3259 (1993)
$\text{CHNRNRCO}_2\text{R}$	$\text{MeOCHNRNRCO}_2\text{R}$, cat Me_3SiOTf	SL 619 (1990)
	$\text{RO}_2\text{CN}(\text{C}_5\text{H}_4)\text{OH}$, Me_3SiOTf	JOC 55 4668 (1990)
	 Br , ZnCl_2 or AgOTf	JACS 110 1547 (1988)
	 ($\text{X} = \text{OMe}, \text{OAc}$), Lewis acid	SL 1149 (1995)
	 RO , Me_3SiOTf	TL 36 4315 (1995)
CH_2SR	ClCH_2SR , cat Me_3SiX ($\text{X} = \text{I}, \text{OTf}$)	CL 405 (1983)
CHRSAr	ROCH_2SR , TiCl_4	JOC 57 5150 (1992)
	$\text{RCH}(\text{SAr})_2$, TiCl_4	JACS 109 7199 (1987) JOC 55 5966 (1990)
	NO_2CHRSPh , SnCl_4	CC 947 (1987)
$\text{CR}_2\text{SR}'$	$\text{R}_2\text{C}(\text{SR}')_2$, FeCl_3 or SnCl_4	TL 4971 (1979) Syn Commun 11 315 (1981) JACS 115 3855 (1993)
$\text{CR}^1(\text{SPh})\text{CHR}^2\text{R}^3$	$\text{R}^1\text{C}(\text{SPh})=\text{CR}^2\text{R}^3$, $\text{ROH} \cdot 2\text{TiCl}_4$	TL 27 3029 (1986)
$\text{CH}(\text{SPh})\text{Sn}(n\text{-Bu})_3$	$n\text{-Bu}_3\text{SnCHClSPh}$, ZnBr_2	TL 30 239 (1989)
$\text{CH}(\text{SPh})\text{CH}=\text{CHSPh}$	$\text{PhSCH}=\text{CHCH}(\text{SPh})_2$, SnCl_4 or TiCl_4	TL 35 5481 (1994)
$\text{CH}(\text{SPh})\text{C}\equiv\text{CR}$	$\text{PhSCH}=\text{C}=\text{CRSnR}_3$, SnCl_4	TL 31 6685 (1990)

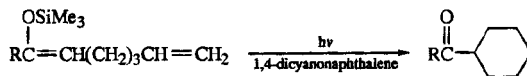
R	Reagents	
CH(SPh) ₂	HC(SPh) ₃ , SnCl ₄	TL 30 1495 (1989)
CH ₂ OH	RLi/H ₂ CO/H ₂ O	JOC 49 3685 (1984)
	RLi/ZnCl ₂ /H ₂ CO/H ₂ O	JACS 110 8483 (1988)
		TL 29 5359 (1988)
CHROH or CR ₂ OH	RCHO or R ₂ CO, various reagents	See page 1317, Section 8.
CHOHCHF ₂	F ₂ CHCH(OH)OEt, ZnCl ₂ or ZnI ₂	JOC 58 2302 (1993)
CH ₃ C(OH)CN	CH ₃ COCN, TiCl ₄	TL 22 1171 (1981)
CH ₂ OCH ₃	ClCH ₂ OCH ₃ , cat (C ₆ F ₅) ₃ B	SL 577 (1993)
CH ₂ OCH ₂ Ph	H ₂ C(OCH ₂ Ph) ₂ , cat Me ₃ SiOTf	TL 28 517 (1987)
	ClCH ₂ OCH ₂ Ph, TiCl ₄	TL 28 517 (1987)
CH ₂ OCHRM ₃ (M = Si, Sn)	CH ₃ OCH ₂ OCHRM ₃ , TiCl ₄ or cat Me ₃ SiOTf	JACS 112 7438 (1990)
CHORR (chiral)	 RCH, TiCl ₄	JACS 104 7371, 7372 (1982); 106 7588 (1984)
		JOC 52 180 (1987)
CHORR	RCH(OR) ₂ , cat TfOH, cat bis-trimethylsilylacetamide or bis-trimethylsilylurea	SL 433 (1993)
	RCH(OR) ₂ , cat FSO ₃ H, cat CH ₃ C(OSiMe ₃)=NSiMe ₃	SL 583 (1993)
	RCH(OR) ₂ , cat (Ph ₃ C)ClO ₄	CL 1759 (1984)
	RCH(OR) ₂ , cat (C ₆ F ₅) ₃ B	SL 577 (1993)
	RCH(OR) ₂ , BF ₃ ·OEt ₂	SL 153 (1991)
		JOC 58 579 (1993)
	RCH(OR) ₂ ,  BOTf	TL 30 1825 (1989)
	RCH(OR) ₂ , AlCl ₃	SL 317 (1990)
		TL 34 7623 (1993)
	RCH(OR) ₂ , Me ₃ SiOTf	TL 26 3629 (1985); 29 685, 695 (1988)
		JOC 55 3982 (1990); 58 579 (1993)
	RCH(OR) ₂ , cat Me ₃ SiN(SO ₂ F) ₂	TL 34 7335 (1993)
	RCH(OR) ₂ , cat Me ₃ SiI	BCSJ 56 3195 (1983)
	RCH(OR) ₂ , cat Me ₃ SiCl, cat SnCl ₄	CL 463 (1987)
	RCH(OR) ₂ , cat SnCl ₂ , cat Ph ₃ CCl	CL 491 (1987)
	RCH(OR) ₂ , SnCl ₄	JOC 57 5078 (1992); 58 579 (1993)
	RCH(OR) ₂ , cat BiCl ₃	TL 29 4719 (1988)
		BCSJ 64 990 (1991)

	RCH(OR)_2 , cat BiCl_3 , cat NaI or ZnI_2	JOC 58 1835 (1993)
	RCH(OR)_2 , cat Sc(OTf)_3	SL 472 (1993)
	RCH(OR)_2 , $i\text{-PrOTfCl}_3$	TL 30 1825 (1989)
	RCH(OR)_2 , $\text{TiCl}_2(\text{O-}i\text{-Pr})_2$	TL 33 6979 (1992) (intramolecular)
	RCH(OR)_2 , TiCl_4	CC 1691 (1986); 876 (1987) (both intramolecular) JACS 108 3513 (1986); 111 6648 (1989); 115 49 (1993) (intramolecular) TL 28 3747 (1987) (intramole- cular); 30 1825 (1989); 31 6625 (1990) (intramolecular); 34 7623 (1993) JOC 54 98 (1989); 55 1114, 3568 (intramolecular), 3982, 6107 (1990); 57 2997, 5150 (intramolecular) (1992); 58 579, 2718 (intramolecular), 6675 (1993)
	RCH(OR)_2 , cat $\text{Rh}_4(\text{CO})_{12}$	TL 28 6657 (1987)
	RCH(OR)_2 , cat [Rh(COD)(dppb)] ClO_4	TL 28 6657 (1987)
	RCH(OR)_2 , cat [Rh(COD)Cl] $_2$, cat Me_3SiCN	CL 1273 (1989)
	RCH(OR)_2 , cat Yb(OTf)_3	Syn 371 (1993)
	ClCHROR , cat Me_3SiX ($\text{X} = \text{I}, \text{OTf}$)	CL 405 (1983)
CR_2OR	$\text{R}_2\text{C(OR)}_2$, cat FSO_3H , cat $\text{CH}_3\text{C(OSiMe}_3\text{)=NSiMe}_3$	SL 583 (1993)
	$\text{R}_2\text{C(OR)}_2$, cat $(\text{Ph}_3\text{C})\text{ClO}_4$	CL 1759 (1984)
	$\text{R}_2\text{C(OR)}_2$, cat Me_3SiI	BCSJ 56 3195 (1983)
	$\text{R}_2\text{C(OR)}_2$, cat Me_3SiOTf	JACS 102 3248 (1980)
	$\text{R}_2\text{C(OR)}_2$, cat $\text{Me}_3\text{SiN(SO}_2\text{F)}_2$	TL 34 7335 (1993)
	$\text{R}_2\text{C(OR)}_2$, cat $n\text{-Bu}_2\text{Sn(OTf)}_2$	JACS 112 901 (1990)
	$\text{R}_2\text{C(OR)}_2$, TiCl_4	CL 15 (1974) JACS 109 527 (1987) (chiral) TL 28 4181, 4847 (1987); 29 3097 (1988) (all chiral) JOC 54 2599 (1989); 57 720, 1412 (1992) (all chiral)
	 , $\text{BF}_3 \cdot \text{OEt}_2$	SL 40 (1990)
	 , $\text{BF}_3 \cdot \text{OEt}_2$, MgBr_2 or ZnBr_2	JOC 54 4100 (1989)
	 , cat $\text{Sc(ClO}_4\text{)}_3$	TL 35 3319 (1994)

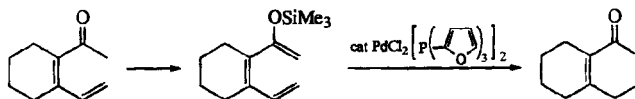
	HC(OR) ₃ , Et ₂ AlCl	SL 829 (1994) (intramolecular)
	HC(OMe) ₃ , cat MeSiOTf	JACS 102 3248 (1980)
	HC(OR) ₃ , cat Me ₃ SiI	BCSJ 56 3195 (1983)
	HC(OR) ₃ , SnCl ₄	TL 25 2813 (1984); 31 301 (1990)
	HC(OMe) ₃ , TiCl ₄	CL 15 (1974)
	MeLi/HC(OMe) ₃ /BF ₃ ·OEt ₂	TL 23 3595 (1982)
CR(OMe) ₂	RC(OMe) ₃ , cat Me ₃ SiOTf	TL 27 5099 (1986) (intramolecular)
	 , Lewis acid	TL 31 2779, 4223 (1990) SL 99 (1990)
CHO	 BF ₄ ⁻ /HgO, BF ₃ ·OEt ₂	TL 22 2829 (1981)
COCH ₃	(CH ₃ CO)BF ₄	JOC 46 3771 (1981)
COR	RCOCl	CC 946 (1972)
	RCOCl, ZnBr ₂ or TiCl ₄	TL 28 6355 (1987)
	RCOCl, ZnCl ₂ or SbCl ₃	Tetr 39 841 (1983)
	RCOCl, TiCl ₄ or SnCl ₄	JOC 47 5099 (1982)
	MeLi/RCOCl	JOC 47 3219 (1982)
		TL 1187 (1977)
		Helv 64 716 (1981)
CO ₂ CH ₃	2 MeLi/chiral HNRR'/CO ₂ /MeI	TL 27 2767 (1986) (chiral)
CONHAr	ArNCO/H ₂ O	JOMC 164 123 (1979)
COSMe	MeLi/COS/MeI	JOC 47 3193 (1982)
halogen	—	See page 709, Section 1.
OH	—	See page 981, Section 7.
OAc	Pb(OAc) ₄ /H ₃ O ⁺	Syn Commun 6 59 (1976)
	Pb(OAc) ₄ , KOAc, HOAc	Tetr 39 861 (1983)
	AgOAc, I ₂	JOC 46 2717 (1981)
O ₂ CPh	Pb(O ₂ CPh) ₄ /(Et ₃ NH)F	JOC 41 1673 (1976)
OMs	PhI(OMs)OH	JOC 54 1101 (1989)
O ₃ SAr	(ArSO ₃) ₂	JOC 50 5148 (1985)
		TL 27 5811 (1986)
	PhI(OTs)OH	JOC 54 1101 (1989)
SAr	PhSCl	CC 946 (1972)
		Tetr 37 4027 (1981)
	RCONRSAr, Me ₃ SiOTf	JOC 57 1948 (1992)
SOR (R = Me, Ph)	RSOCl	Syn 283 (1982)
NO ₂	C(NO ₂) ₄	TL 34 1859 (1993)



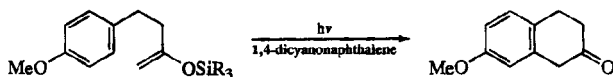
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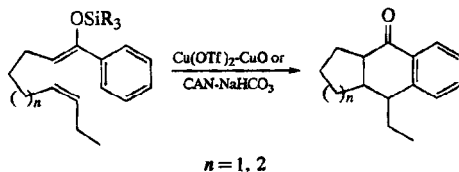
TL 33 1973 (1992)



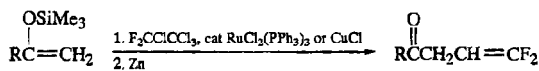
JACS 113 4903 (1991)



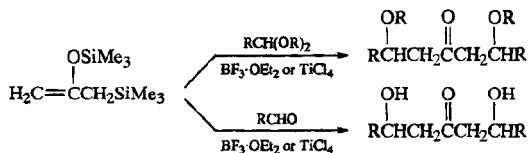
TL 34 6631 (1993)



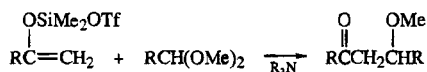
JOC 55 4786 (1990); 57 2399 (1992)



JOC 58 5163 (1993)



JOC 54 3254 (1989)



JOC 58 2647 (1993)


 Pb(OAc)₄

TL 28 873 (1987)

 VO(OR)Cl₂ (R = Et, *i*-Pr)

TL 33 5823 (1992)

 Cu(OTf)₂

TL 3741 (1977); 3555 (1978)

Chem Pharm Bull 28 262 (1980)

 Ag₂O

JACS 97 649 (1975)

 PhIO, BF₃·OEt₂

CC 420 (1985) (R = Ar)

JACS 116 8784 (1994)

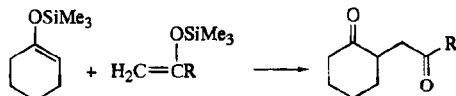
 (PhIOPh)(BF₄)₂

TL 29 3717 (1988)

JOC 54 2609 (1989)

 (PhIOPh)(PF₆)₂

JOC 54 2609 (1989)


 VO(OEt)Cl₂

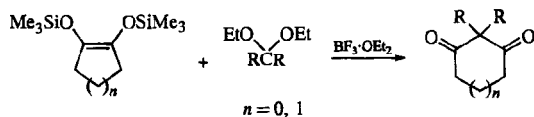
TL 33 5823 (1992)

CAN

TL 30 3707 (1989)



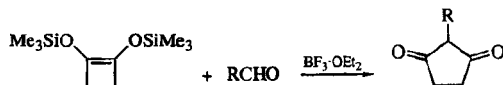
TL 33 5823 (1992)



JACS 99 961 (1977); 106 1759 (1984)

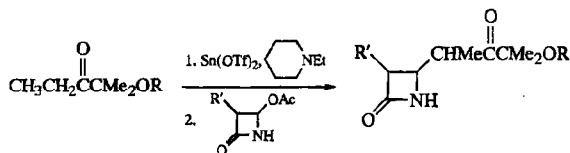
Org Syn 65 17 (1987)

TL 29 4369 (1988); 30 1021 (1989)

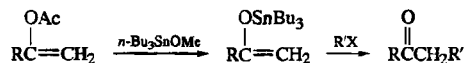
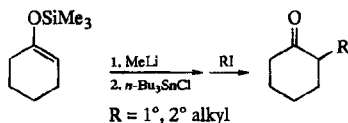


TL 30 4185 (1989)

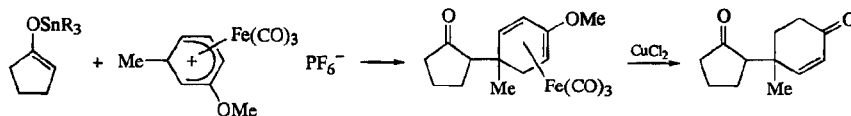
8. Enol Stannanes and Related Compounds



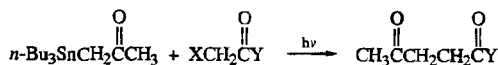
JOC 52 5491 (1987)

JOMC 55 273 (1973) ($R' = \text{Me, Et, PhCH}_2, \text{CH}_2\text{CH}=\text{CH}_2$)TL 3791 (1977) ($R' = 1^\circ \text{ RD}$); 21 2591 (1980) [$R'X = \text{allylic OAc, cat Pd(PPh}_3)_4$]CL 939 (1982) [$R'X = \text{ArBr, cat PdCl}_2(\text{PAr}_3)_2$]JACS 109 7223 (1987) [$R'X = \text{heterocyclic iodide, cat Pd(OAc)}_2\text{-(}o\text{-Tol)}_3\text{P}$]JOC 59 4386 (1994) [$\text{RCOCH}_2\text{Br, RC(=NR)CHRX}$]

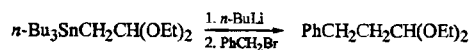
TL 1117 (1969)



JOC 54 4663 (1989)

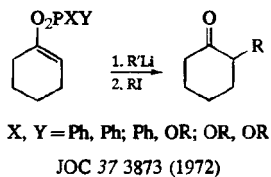
 $X = \text{Br, I, SePh; } Y = \text{R, OR}$

TL 31 6669 (1990)

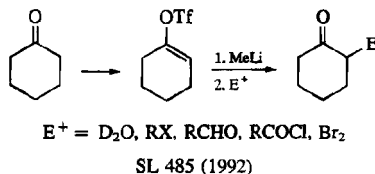


JOMC 212 C31 (1981)

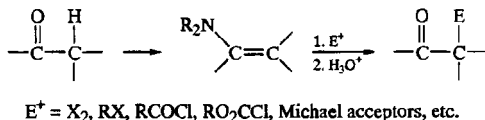
9. Enol Phosphorus Compounds



10. Enol Triflates



11. Enamines



Reviews:

Adv Org Chem 4 1 (1963)

"Enamines: Synthesis, Structure and Reactions," Ed. A. G. Cook, Marcel Dekker, New York (1969);
2nd ed. (1987)

Syn 510 (1970); 517 (1983)

S. F. Dyke, "The Chemistry of Enamines," Cambridge Univ. Press, New York (1973)

Org Syn 53 48, 59 (1973)

Org Syn Coll Vol 5 808 (1973)

Acta Chem Scand B 32 335 (1978)

Tetr 38 1975, 3363 (1982)

"The Chemistry of Enamines," Parts 1 and 2, Ed. Z. Rappoport, J. Wiley, Chichester, U.K. (1994)

E^+

RX

π -allylpalladium compounds (intramolecular, chiral)

JACS 85 207 (1963)

CC 469 (1986)

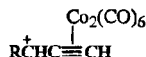
TL 30 1543 (1989); 31 3623 (1990)

Heterocycles 30 283 (1990)

Chem Pharm Bull 39 616 (1991)

JOC 59 203 (1994)

See page 594, Section 8.



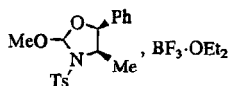
E^+ $RCH(OR)_2, BF_3 \cdot OEt_2$

BCSJ 57 1876 (1984)

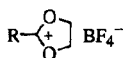
 $HC(OR)_3$, Lewis acid

CL 1307 (1982)

BCSJ 57 1876 (1984)



TL 31 4223 (1990)



CL 1243 (1987)

 $RCOCl$

JACS 85 207 (1963)

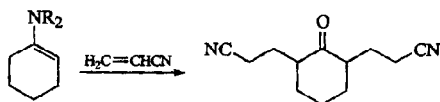
JOC 58 6072 (1993)

 R_fCOCl

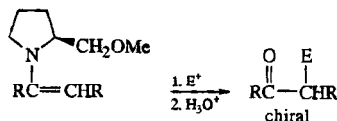
TL 36 3145 (1995)

 X_2

See page 709, Section 1.



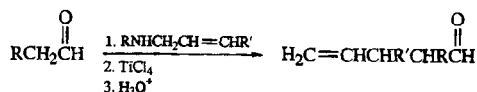
TL 34 2067 (1993)

 E^+ R_fI , Zn, Cp_2TiCl_2 , ultrasound ($E = R_f$)

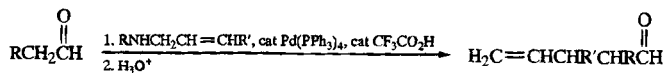
JACS 107 5186 (1985)

 $ArCH=CHNO_2$ (conjugate addition)

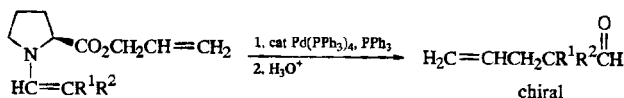
Helv 65 1637 (1982)



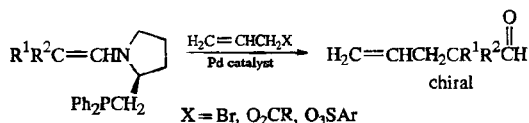
TL 4337 (1978); 30 5341 (1989)



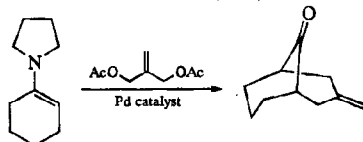
JOC 53 4489 (1988)



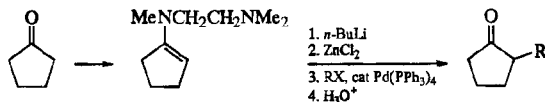
TL 30 1543 (1989)



TL 31 3623 (1990)

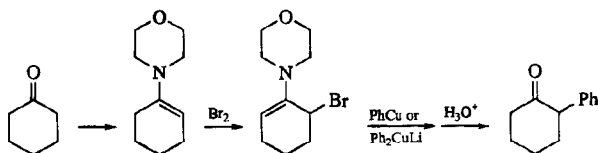


TL 29 5663 (1988)



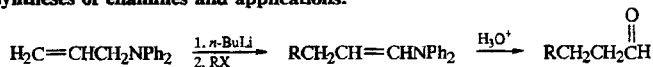
R = aryl, vinylic

CL 1007 (1987)

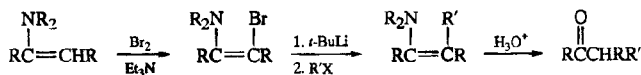


JOC 52 3696 (1987)

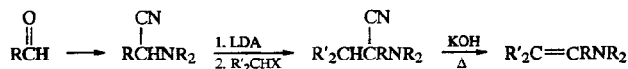
Alternate syntheses of enamines and applications:



JOC 56 2955 (1991)



BSCF II 297 (1982)



Syn 127 (1979)



TL 21 2671 (1980)



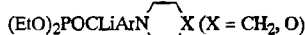
TL 2433 (1979)



JOC 39 2814 (1974); 42 2520 (1977); 44 3391 (1979)



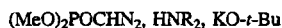
JOC 41 3337 (1976); 42 2520 (1977)



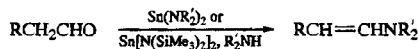
Arch Pharm 305 88 (1972)



Ann 686 107 (1965)

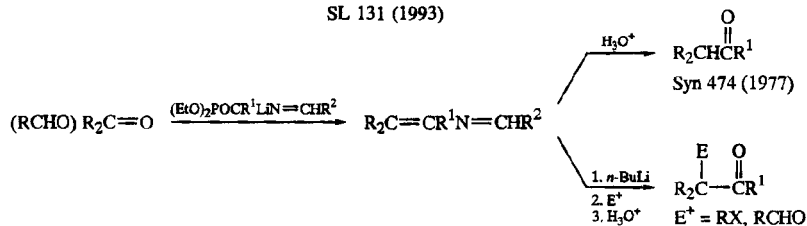


TL 21 2041 (1980)



JOC 57 5063 (1992)

SL 131 (1993)



JOC 43 782, 3792 (1978); 44 3391 (1979); 46 3567 (1981); 47 1513 (1982); 52 1962 (1987); 59 8115 (1994)

JACS 102 5866 (1980); 106 6431 (1984)

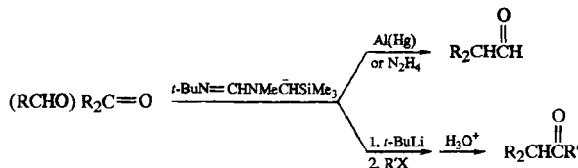
Syn Commun 11 429 (1981)

Org Syn 65 119 (1987)

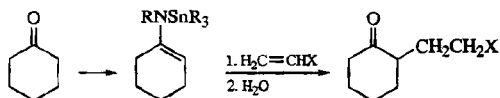
TL 28 503 (1987)

Org Syn Coll Vol 8 451 (1993)

See also page 1546, Section 23.



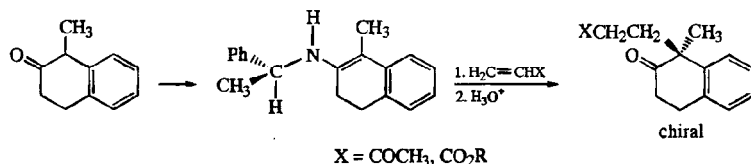
JACS 104 877 (1982)



X = CO₂R, CN

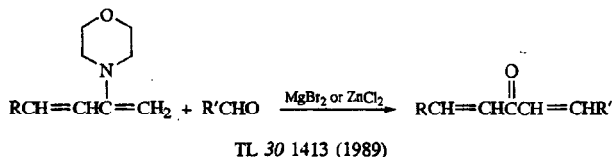
JOMC 186 C9 (1980)

TL 21 4511 (1980)

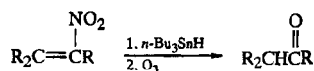


JACS 107 273 (1985)

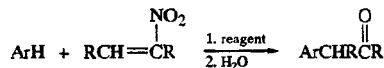
TL 28 2367 (1987); 30 6511 (1989); 31 875, 879 (1990)



12. Nitroalkenes



JOC 55 2070 (1990)



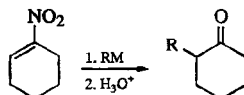
Reagent

$\text{CF}_3\text{SO}_3\text{H}$

JOC 54 733 (1989)

TiCl_4

TL 29 2977 (1988)



RM

$\text{RCOCHRCOR}, \text{KF}$

CC 726 (1975)

JOC 42 2779 (1977)

Syn 407 (1980)

$\text{RCOCHRCO}_2\text{R}, \text{KF}$

Syn 407 (1980)

RCOCHRLi

Syn 563 (1990)

$\text{LiCHRCO}_2\text{Li}$

CL 1505 (1982)

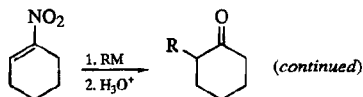
JOC 49 2857 (1984)

$\text{LiCHRCO}_2\text{R}$

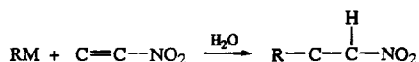
JOC 49 2857 (1984)

R_3Al

JOC 53 45, 2614 (1988); 54 2391 (1989)

RM

R_4AlMgX	IOC 54 2391 (1989)
$H_2C=CRCH_2SiMe_3, AlCl_3$	TL 22 1115 (1981)
$H_2C=CROSiMe_3; AlCl_3, SnCl_4$ or $TiCl_4$	JACS 106 2149 (1984)
$RCH=C(OSiR_3)OR, TiCl_4, Ti(O-i-Pr)_4$	CL 1043 (1980) JACS 106 2149 (1984)
$RCH=C=CHSnPh_3, TiCl_4$ ($R = CHRC\equiv CH$)	IOC 55 4853 (1990)
$RCu(CN)ZnI$	IOC 54 5200 (1989); 57 5431 (1992)

RM

RCH_2NO_2, Et_3N	TL 29 6001 (1988)
$RCOCHRCOR, KF$	CC 726 (1975) IOC 42 2779 (1977) Syn 407 (1980)
$RCOCHRCO_2R, KF$	Syn 407 (1980)
$LiCHRCOCLiCOX$ ($X = H, R, OR$)	Ber 108 1961 (1975)
$RCOCH_2R, Sn(OTf)_2, N$ -ethylpiperidine	CL 855 (1985)
$RCOCHRLi$	Ber 108 1924 (1975) Helv 62 1710 (1979) Chimia 38 255 (1984) CL 239 (1990)
$RO_2CCHRLi$	Ber 108 1924 (1975) Chimia 38 255 (1984)
$RO_2CCRLiCHROLi$	Helv 63 2005 (1980)
$RN(Li)COCHRLi$	Ber 108 1961 (1975)
$R_2NCOCHRLi$	Angew Int 10 501 (1971) Ber 108 1924 (1975)
$Me_3SiOCR=CHR, Cl_2Ti(O-i-Pr)_2$	Helv 68 319 (1985)
enamine	Tetr 24 1889 (1968); 29 3011 (1973); 30 2741 (1974) Helv 64 1413 (1981); 65 1637 (1982); 68 162 (1985)
$MeN(NO)CH_2Li$	Ber 108 1924 (1975) Helv 62 1710 (1979)



(MeS)₃CLi

RLi

RMgX

RCH=CHAlR₂

RCH=CHCH₂SiR₃, TiCl₄

RCH=CHCH₂SnR₃, AlCl₃, TiCl₄, or
TiCl₂(O-*i*-Pr)₂

ROCH=CHCH₂SnR₃, TiCl₄
(R = CH(OR)CH=CH₂)

RCH=C=CHSnR₃, TiCl₄ (R = CHRC≡CH)

R₂CuLi

RCu(CN)ZnX

RZnX

R₃ZnLi

Ber 108 1924 (1975)

Helv 62 1710 (1979)

Ber 108 1924 (1975)

JOC 43 2460 (1978)

Helv 62 1710 (1979)

TL 24 2795 (1983)

JCS 1494, 1497 (1947)

JACS 100 6294 (1978)

Syn 379 (1988)

Tetr 43 5411 (1987)

BCSJ 59 1267 (1986)

Syn 471 (1987)

JOC 53 3597 (1988)

JOC 53 3597 (1988)

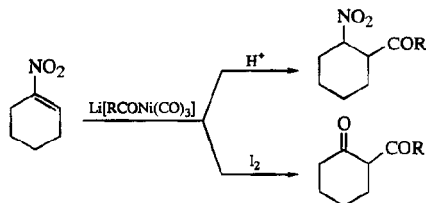
JOC 55 4853 (1990)

Helv 62 1710 (1979)

JOC 57 5431 (1992)

JCS 1497 (1947)

Helv 62 1710 (1979)



JOC 60 1900 (1995)

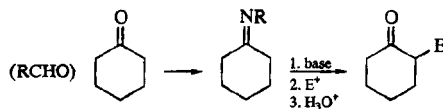
13. Imines

Reviews:

"The Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, London (1970)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 2, Part 1.16, p 475

See also page 1507, Section 11; and page 1546, Section 23.

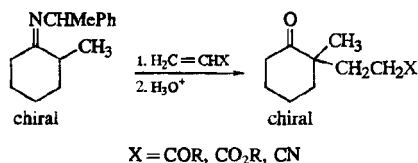
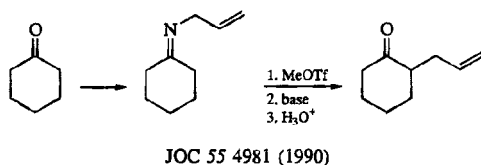
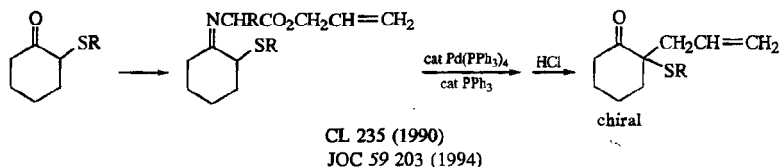


$E^+ = RX, RCHO, R_2CO, \text{epoxide, Michael acceptors}$

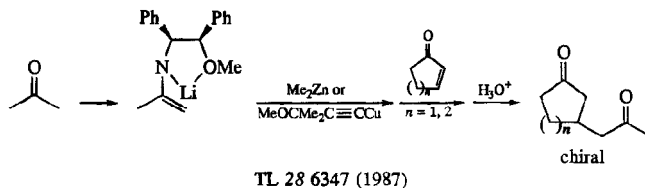
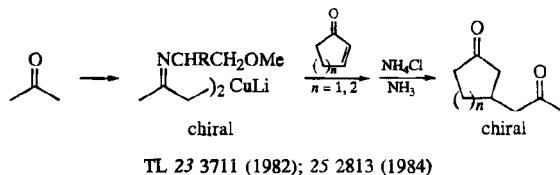
Review: Syn 517 (1983)

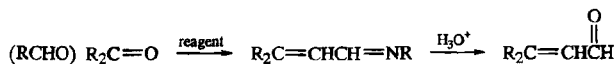
- | | |
|----------------------|---|
| metallation | JACS 115 8008 (1993) |
| alkylation | JACS 85 2178 (1963); 92 7593 (1970); 93 5938 (1971); 100 7999 (1978); 102 1426, 5866 (1980); 104 2081 (1982); 105 4396 (1983) (regioselectivity); 111 995 (1989)
Helv 50 2440 (1967)
BSCF 3976 (1970)
Organomet Chem Syn 1 237 (1971)
TL 1237 (1974); 24 257, 511 (chiral), 3559 (regioselectivity) (1983); 29 3207 (1988); 32 3879 (1991); 35 3763 (1994)
JOC 39 3102 (1974); 42 2545 (1977); 46 3157 (regioselectivity), 4631 (1981); 56 1210 (1991); 58 132, 356, 5931 (1993); 60 6123 (1995)
Ann 719 (1975)
CC 47 (1979)
Tetr 35 1745 (1979); 48 3735 (1992)
Can J Chem 60 1836 (1982) (chiral); 61 2466 (1983)
Org Syn Coll Vol 6 526, 818 (1988)
SL 285 (1994) |
| epoxide opening | JOC 32 1679 (1972)
Ann 1075 (1973)
Syn 256 (1975) |
| directed aldol | Angew Int 2 683 (1963); 7 7 (1968)
Ber 97 3548 (1964)
Helv 50 2440 (1967)
Rec Chem Prog 28 45 (1967)
JOC 34 1122 (1969)
JCS C 460 (1969)
TL 381 (1970)
Bull Acad Sci USSR, Div Chem Sci 25 2465 (1976)
JACS 102 5866 (1980)
Org Syn Coll Vol 6 901 (1988) |
| Michael additions | Tetr Asym 3 459 (1992) (chiral, review)
JOC 59 5100 (1994) |
| regiochemistry | JACS 100 292 (1978); 104 2081 (1982)
JOC 43 782, 3792 (1978) |
| asymmetric induction | BSCF 4571 (1968)
Chem Pharm Bull 22 459 (1974); 27 2760 (1979) |

JACS 98 3032 (1976); 103 3081, 3088 (1981)
 JOC 42 377 (1977); 43 892, 3245 (1978)
 TL 573 (1978); 3929 (1979); 24 511 (1983)
 Angew Int 18 221 (1979)
 Tetr Asym 3 459 (1992) (review)



JACS 107 273 (1985); 110 958 (1988) (intramolecular)
 TL 26 2577 (1985); 28 2367 (1987); 29 2667 (1988); 30 2645, 4121 (1989); 35 9705 (1994)
 SL 89 (1992); 529 (1995)
 Tetr Asym 3 459 (1992) (review)
 JOC 59 311 (1994)

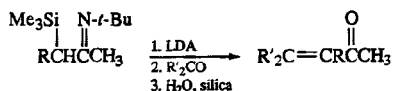


Reagent

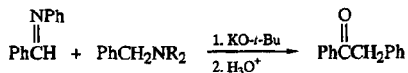
JCS C 460 (1969)
 JOC 43 3788 (1978)



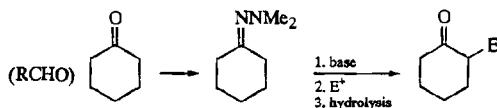
TL 7 (1976); 24 2481 (1983); 26 2391 (1985); 27
 6177 (1986); 28 259 (1987)
 JOC 45 2013 (1980); 50 2798 (1985)



TL 24 2481 (1983)



TL 32 1617 (1991)

14. Hydrazones**Reviews:**

Syn 517 (1983)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991),
 Vol 2, Part 1.17, p 503

preparation of dimethylhydrazones

Ber 111 1337 (1978)

deprotonation

TL 3691 (1978); 4145, 4149 (1979); 21 3115
 (1980)
 JACS 101 5654 (1979); 111 6772 (1989); 115 8008
 (1993)

hydrolysis

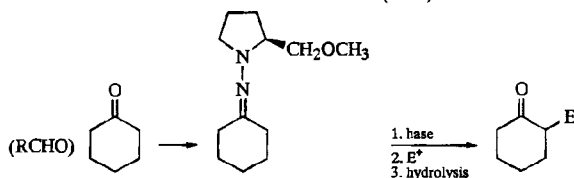
TL 3 (1976)

electrophile:

RX

JACS 93 5938 (1971); 101 5654 (1979); 106 4865
 (1984); 107 2078 (stereoselectivity), 5303 (1985);
 110 5172 (1988); 111 3363 (1989); 115 830,
 11446 (1993); 117 10449 (1995)

	TL 3, 11, 4687 (1976); 3305 (1977); 4145, 4149 (1979); 27 2595 (1986); 28 813, 5275 (1987); 29 4053 (1988); 30 6081 (1989); 32 1027 (1991); 35 3255 (1994) Ber 111 1337 (1978) JOC 46 4631 (1981); 51 3405, 4212 (1986); 52 5548 (1987); 56 1393, 2086 (1991); 58 5931 (1993) SL 901 (1992)
RX, CuCN	TL 30 1125 (1989)
epoxide	TL 11 (1976) Ber 111 1362 (1978) JOC 54 2183 (1989); 57 353 (1992) JACS 113 7613 (1991)
RCHO, R ₂ CO	TL 11 (1976) Ber 111 1362 (1978) Angew Int 21 864 (1982) (titanium species) Ann 1439 (1983)
enone, CuX (1,4-addition)	TL 11 (1976); 21 3115 (1980) Ber 111 1362 (1978)
RCOCl	TL 2853 (1978)
RCON(Me)OMe	JOC 54 4229 (1989); 55 6260 (1990) JACS 112 7001 (1990); 115 11446 (1993)
I ₂ (1,4-alkanedione)	TL 11 (1976) Ber 111 1362 (1978)
Me ₃ SiCl	TL 7 (1976) Ber 111 1362 (1978) JACS 112 8120 (1990)
MeSSMe	TL 4687 (1976)



Reviews:

Chemtech 11 504 (1981)

D. Enders in "Current Trends in Organic Synthesis," Ed. H. Nozaki, Pergamon Press, Oxford (1983), p 151

D. Enders in "Selectivity-a Goal for Synthetic Efficiency," Eds. W. Bartmann, B. M. Trost, Verlag Chemie, Weinheim (1984), p 65

D. Enders in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Chpt 4 (Alkylation of Chiral Hydrazones)

Chem Scripta 25 139 (1985)

Org Syn Coll Vol 8 403 (1993)

E^+

RX

Angew Int 15 549 (1976); 18 397 (1979)
 TL 191 (1977); 29 1269, 4333, 4481 (1988); 30 6081
 (1989); 32 537 (1991); 34 2453 (1993)
 Ber 112 2933 (1979)
 Acta Chem Scand B 35 555 (1981)
 Tetr 38 3705 (1982); 40 1345 (1984)
 Ann 1439 (1983)
 Org Syn 65 183 (1987)
 CC 358 (1987)
 JOC 55 2800 (1990); 58 4881 (1993)
 JACS 112 8090 (1990)
 SL 897, 901, 999 (1992); 792 (1994)
 Org Syn Coll Vol 8 403 (1993)

RCHO, R_2CO

Angew Int 17 206 (1978)
 Ber 112 3703 (1979)

ArCH=CHNO₂ (1,4-addition)

Helv 65 1637 (1982)

RCH=CHCO₂R (1,4-addition)

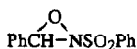
TL 24 4967 (1983); 27 3491 (1986)
 Ber 120 1223 (1987)
 JOC 54 3963 (1989)

ClCO₂R

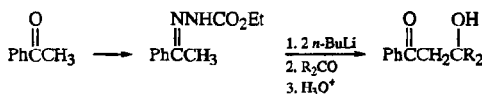
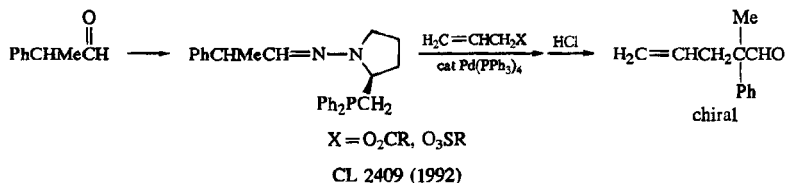
SL 891 (1992)

MeNCS

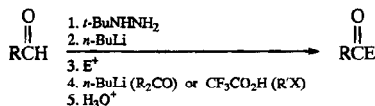
TL 33 7211 (1992)



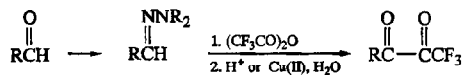
TL 29 2437 (1988)



TL 24 3239 (1983)

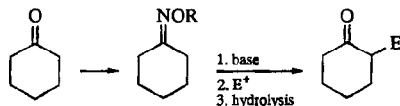
 $E^+ = \text{R'X}, \text{R}_2\text{CO}$

CC 1040 (1983)



JOC 53 129, 519 (1988)

15. Oxime Ethers



preparation of oximes

TL 1415 (1978)

deprotonation

TL 3889 (1975); 1415 (1978); 2I 3115 (1980)

electrophile:

RX

CC 674 (1976)

TL 3I 5881 (1990)

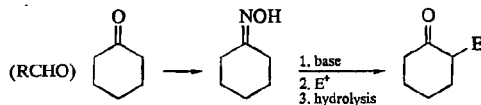
 R_2CO

TL 1415 (1978)

enone, CuBr (1,4-addition)

TL 2I 3115 (1980)

16. Oximes



deprotonation

TL 1439 (1976)

electrophile:

RX

JACS 9I 676 (1969)

TL 1439, 4431 (1976)

JOC 4I 439 (1976)

JOMC 165 1 (1979)

epoxide

JOMC 177 35 (1979)

 RCHO , R_2CO

JOC 4I 439 (1976)

J Heterocyclic Chem 13 449 (1976)

JOMC 165 1 (1979)

 RCOCl (to isoxazole)

J Heterocyclic Chem 13 607 (1976)

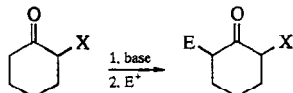
 RCO_2R (to isoxazole)

JOC 35 1806 (1970)

 RCONR_2 (to isoxazole)

JOC 43 3015 (1978)

17. Blocking Groups

X=CHNR₂

JCS 501 (1944); 582 (1945)

JACS 74 4223 (1952)

=CHOR

JACS 69 1361 (1947)

=CHSR

JOC 27 1615, 1620 (1962); 32 1741 (1967)

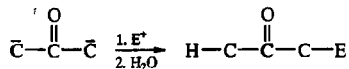
JACS 105 6975 (1983)

TL 31 4343 (1990)

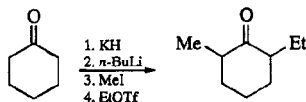
(SR)₂

JCS 1131 (1957)

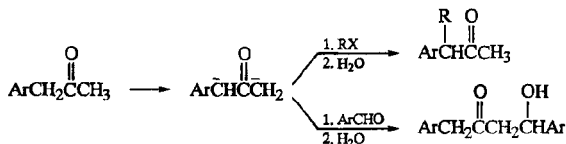
18. Alkylation and Acylation of Carbonyl Dianions

 $E^+ = \text{RX, RCHO, epoxide, RCO}_2\text{R}$

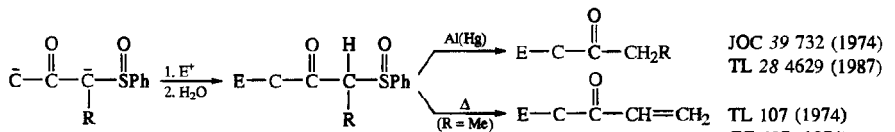
JACS 102 2110 (1980)



JOC 59 245 (1994)

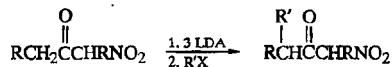


JOC 48 2957 (1983)

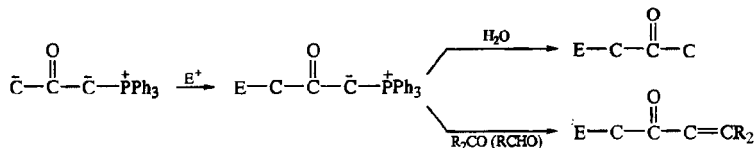
 $E^+ = \text{RX, epoxide, RCHO, R}_2\text{CO, RCH=CHCO}_2\text{R (Michael addition)}$

TL 28 5677 (1987)

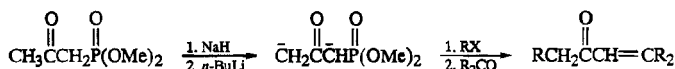
JOC 39 732 (1974)
TL 28 4629 (1987)TL 107 (1974)
CC 497 (1974)
JACS 106 721 (1984)



SL 64 (1992)

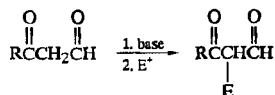

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCO}_2\text{R}$

JOC 38 4082 (1973); 41 509 (1976)



JOC 38 2909 (1973)

19. Alkylation and Acylation of β -Ketoaldehydes


 E^+

RX

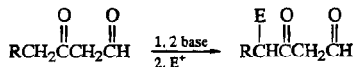
 JACS 69 1361 (1947); 79 6313 (1957)
 JCS 1373 (1954)

 $(\text{Me}_3\text{S})\text{BF}_4$

JOC 48 1362 (1983)

 $\text{ArPb}(\text{OAc})_3, \text{py}$

Austral J Chem 36 789 (1983)


 E^+

RX

JACS 84 1750 (1962); 85 3273 (1963); 87 82, 3186 (1965)

Org Syn 48 40 (1968)

Org Rxs 17 155 (1969) (review)

TL 24 4769 (1983)

 $\text{RCHO}, \text{R}_2\text{CO}$

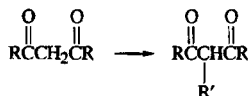
JACS 84 1750 (1962); 87 3186 (1965)

enone (Michael addition)

JACS 87 3186 (1965)

 RCO_2R

JACS 87 3186 (1965)

20. Alkylation and Acylation of β -Diketones

Reviews:

kinetics and thermodynamics

JACS 107 2091 (1985)

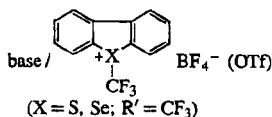
ion pairing and reactivity

JACS 100 3514 (1978); 106 6759 (1984)

O vs C alkylation

Tetr 27 4777 (1971)

Reagent(s):



TL 31 3579 (1990)

JACS 115 2156 (1993)

NaH / (Me₃S)BF₄

JOC 48 1362 (1983)

Triton B, MeI

Org Syn Coll Vol 8 312 (1993)

NaOH, H₂C=CHCH₂Br

JACS 114 3028 (1992)

NaOH, R'X, R₄NX (chiral, phase transfer)

BCSJ 52 3119 (1979)

KOH, R'X

JCS 803 (1953)

Angew 67 783 (1955)

KOH, Cu, R'X (R' = allylic)

Ber 85 1061 (1952)

K₂CO₃, MeI

Org Syn Coll Vol 5 785 (1973)

JOC 59 3786 (1994)

K₂CO₃, EtI

JACS 114 6227 (1992)

K₂CO₃, R'X

Tetr 38 1279 (1982)

K₂CO₃, R'X, *n*-Bu₄NBr

Syn 688 (1989)

K₂CO₃, R'X (R' = benzylic, allylic), cat
CoCl₂(PPh₃)₂

TL 29 1469 (1988)

K₂CO₃, ArI, cat CuI, DMSO

JOC 58 7606 (1993)

Cs₂CO₃, *p*-AcOCH₂C₆H₄OAc
(R' = *p*-CH₂C₆H₄OAc)

TL 33 5287 (1992)

MOEt (M = Li, Na, K, Cs) / R'X

JACS 100 3514 (1978)

NaOMe / R'X

Ber 85 61 (1952)


JCS 811 (1953)

Tetr 2 88 (1958)

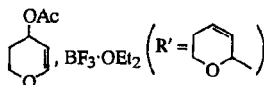
NaOEt / R'X

TL 593 (1965)

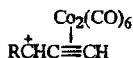
JOC 60 3074 (1995)

KO- <i>t</i> -Bu/R'X	JCS C 1973 (1966)
TIOEt/R'I	JACS 90 2421 (1968) JOC 60 3074 (1995)
DBU, R'X	BCSJ 52 1716 (1979)
 (R ₄ N)N / R'X	JOC 53 907 (1988); 60 3074 (1995)
R ₄ NF, R'X	JCS Perkin I 1743 (1977) CC 64 (1977)
<i>n</i> -Bu ₄ NCl, KF·2H ₂ O, MeI, CH ₃ CN	CC 514 (1979)
KF, Celite, R'X	CL 45 (1979) Syn Commun 11 913 (1981)
KF, Al ₂ O ₃ , R'X	CL 755 (1979)
KF, ion exchange resin, MeI	JOC 54 4993 (1989)
F ⁻ on basic anion exchange resin, R'X	Can J Chem 57 2629 (1979)
Me ₃ SiCH ₂ CH=CH ₂ , CAN	JOC 60 856 (1995)
base/ π -allylpalladium compound (R' = allylic)	J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980) (review) Acct Chem Res 13 385 (1980) (review) R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985) (review)
base/allylic carboxylate, Pd catalyst (R' = allylic)	CC 1162 (1982) (chiral) JOC 53 113 (1988); 54 2759 (1989) (both chiral) TL 30 3109 (1989); 32 2025 (1991)
H ₂ C=CHCH ₂ OAc, KF, cat Pd ₂ (DBA) ₃ ·CHCl ₃ , cat chiral ligand	JACS 114 2586 (1992) (chiral)
NaH/ROCH=CHCH ₂ OAc, cat Pd(PPh ₃) ₄ [R' = ROCH=CHCH ₂ , H ₂ C=CHCH(OR)]	TL 36 535 (1995)
H ₂ C=CHCH ₂ OCO ₂ Me, cat Pd(OAc) ₂ , cat PPh ₃	JOC 59 5847 (1994)
ROCH=CHCH ₂ OCO ₂ R, cat Pd(PPh ₃) ₄ [R' = ROCH=CHCH ₂ , H ₂ C=CHCH(OR)]	TL 36 535 (1995)
R ₂ C=CHCHROAc, cat CoCl ₂	TL 34 6301 (1993)
H ₂ C=CHCR ₂ OH, Triton B	JOC 53 3178 (1988)
RCH=CHCH ₂ OH, cat Co(III) dimethylglyoxime, HOAc	TL 36 6761 (1995)
R'OH, cat Pd(acac) ₂ , cat PPh ₃ , (R' = allylic, benzylic)	Tetr 37 3009 (1981)
H ₂ C=CHCHArOH, cat Pd(PPh ₃) ₄ (R' = ArCH=CHCH ₂)	TL 35 8013 (1994)
R'OH, H ₂ O (R' = 3° allylic, rearrangement)	TL 35 2021 (1994)

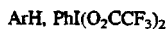
- $p\text{-HOC}_6\text{H}_4\text{CH}_2\text{OH}$, H_2O ($\text{R}' = p\text{-HOC}_6\text{H}_4\text{CH}_2$) JOC 53 891 (1988)
 $i\text{-PrOH}$, BF_3 ($\text{R}' = i\text{-Pr}$) JOC 32 2615 (1967)
 $\text{H}_2\text{C}=\text{CHR}$; PbO_2 , AgO or Ag_2O Syn 454 (1977)
 ($\text{R}' = \text{CH}_2\text{CH}_2\text{R}$)
 $\text{H}_2\text{C}=\text{CHR}$, $\text{Mn}(\text{OAc})_3$ or $\text{Mn}(\text{acac})_3$ JOC USSR 12 1183 (1976)
 ($\text{R}' = \text{CH}_2\text{CH}_2\text{R}$)
 $(\text{CH}_3)_2\text{C}=\text{CH}_2$, HClO_4 ($\text{R}' = t\text{-Bu}$) TL 3599 (1966)



CC 68 (1983)



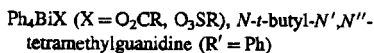
See page 594, Section 8.



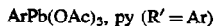
JACS 116 3684 (1994)



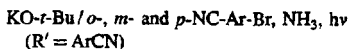
TL 30 5323 (1989) (intramolecular)



TL 23 3365 (1982)



Austral J Chem 32 1561 (1979)



Tetr 38 3479 (1982)



TL 30 1373 (1989)



JOC 53 4149 (1988) (intramolecular)



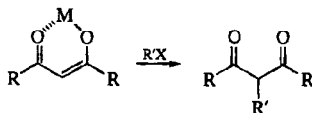
JOC 60 3074 (1995)



Org Syn Coll Vol 6 36 (1988)



TL 34 8457 (1993)

MR'

Na

1° alkyl

JOC 60 3074 (1995)

Tl

1° alkyl

JOC 60 3074 (1995)

Co

3° alkyl, benzylic, allylic

Syn 348 (1979)
 TL 26 3735 (1985); 29 1469
 (1988)
 Tetr 42 4253 (1986)

Cu

3° alkyl, benzylic, allylic

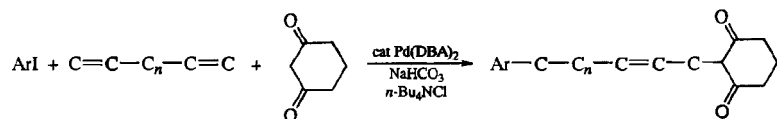
TL 31 7489 (1990)

Zn

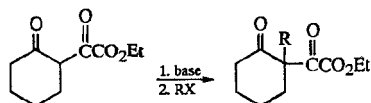
benzylic

TL 26 3735 (1985)

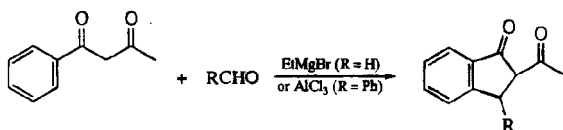
See also the previous equation.



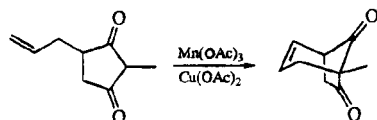
JOC 56 4589 (1991)



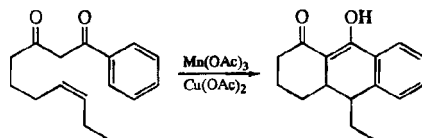
JACS 80 5220 (1958)



TL 34 7339 (1993)

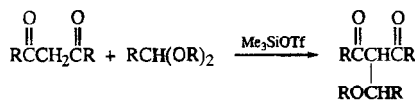


JOC 55 2427 (1990)

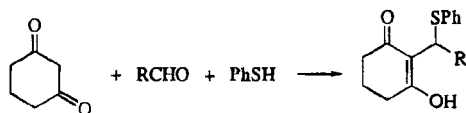


TL 28 845 (1987)

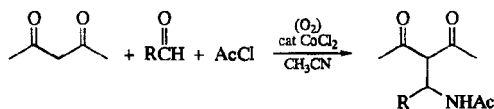
JOC 57 4195 (1992)



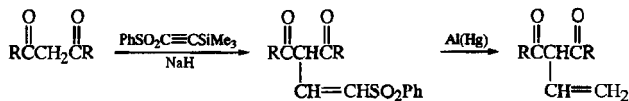
JOC 53 5540 (1988)



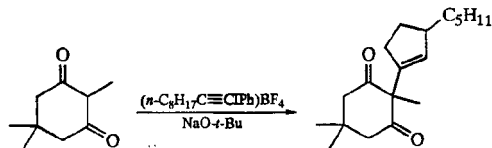
JOC 59 528 (1994)



TL 36 4877 (1995)

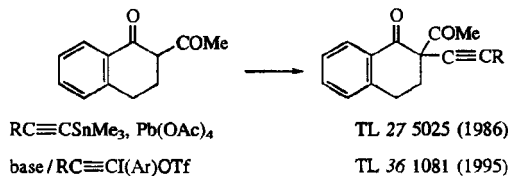


JOC 47 4713 (1982)



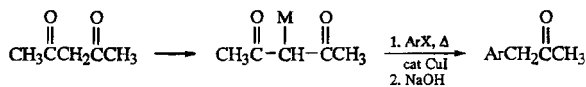
JACS 108 8281 (1986)

TL 36 1081 (1995)



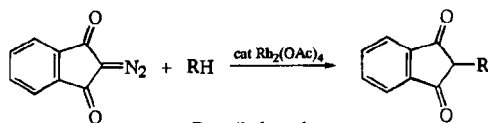
TL 27 5025 (1986)

TL 36 1081 (1995)



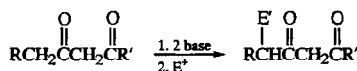
M = Na, K

CL 597 (1982)



R = alkyl, aryl

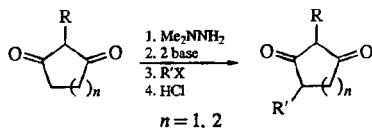
JOC 53 2699 (1988); 59 1945 (1994) (intramolecular)

 E^+

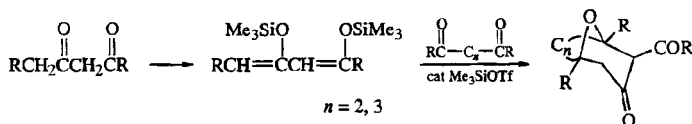
RX

JACS 80 6360 (1958); 81 1160 (1959); 96 1082 (1974)

- JOC 25 158, 1110 (1960); 30 61 (1965); 31 663, 1035 (1966); 57 3365 (1992); 60 2283 (1995)
 BCSJ 40 2698, 2909 (1967)
 Org Syn 47 92 (1967)
 Org Rxs 17 155 (1969) (review)
 Org Syn Coll Vol 5 848 (1973)
 TL 28 1997 (1987)
- Ph_2ICl ($\text{E}' = \text{Ph}$) JOC 29 3511 (1964)
 Org Syn Coll Vol 6 928 (1988)
- $\text{RCH}=\text{CHCOX}$ ($\text{X} = \text{R}, \text{OR}$) (Michael addition) JOC 26 1344 (1961); 28 2266 (1963)
- $\text{RCHO}, \text{R}_2\text{CO}$ JACS 80 6360 (1958)
 JOC 26 1344, 1716 (1961); 30 1007 (1965); 57 3365 (1992)
 BCSJ 40 2909 (1967)
 TL 28 1997 (1987); 33 437 (1992)
- RCO_2R JACS 80 6360 (1958); 94 8253 (1972); 95 6865 (1973); 98 6065 (1976); 99 1631 (1977)
 JOC 25 538, 1110 (1960); 28 725, 2266 (1963); 30 1007, 4263 (1965); 46 2260 (1981); 51 4254 (1986)
 BCSJ 40 2909 (1967)
 Ber 114 2786 (1981)
 Syn Commun 12 621 (1982)
 TL 28 5615 (1987) (5-alkaneolactone)
- $\text{CH}_3\text{CON}(\text{Me})\text{OMe}$ ($\text{E}' = \text{CH}_3\text{CO}$) TL 24 1851 (1983)
- CO_2 JACS 80 6360 (1958)
 JOC 25 1110 (1960); 31 1032 (1966)

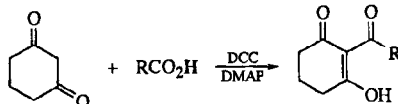


TL 30 1705 (1989)

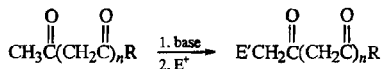


JOC 56 2617 (1991)

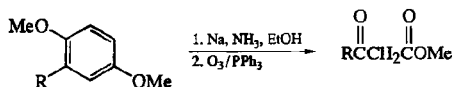
JACS 115 830 (1994)



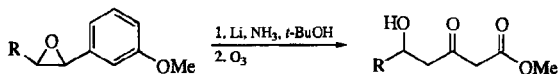
JOC 59 4749 (1994)

21. Alkylation and Acylation of β -Polyketones

n	E^+	
2	RX, RCHO, R ₂ CO RCO ₂ R	JOC 30 4263 (1965) JOC 30 4263 (1965); 46 2260 (1981) JACS 85 3884 (1963); 93 6708 (1971); 94 8253 (1972); 95 6865 (1973) CC 442 (1979)
	CO ₂	JOC 30 4263 (1965) JACS 89 6734 (1967); 91 517 (1969); 98 7733 (1976); 99 1631 (1977)
2, 3	CH ₃ CON(Me)OMe (E' = COCH ₃)	TL 24 1851 (1983)
3	RCO ₂ R CO ₂	JACS 93 6708 (1971); 95 6865 (1973) JACS 93 6708 (1971)

22. Synthesis of β -Keto Acids, Esters, Amides, Imides and Nitriles and DecarboxylationReview: Chem Rev 95 1065 (1995) (β -keto esters)

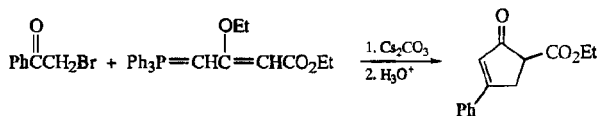
SL 253 (1990)



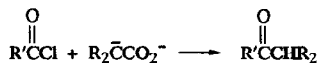
JOC 56 741 (1991)



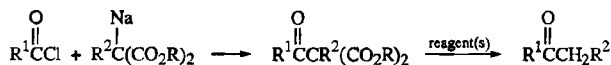
See page 1690, Section 3.



JOC 59 111 (1994)



See page 1386, Section 2.5.



Reagent(s)

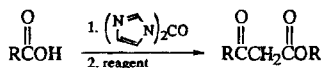
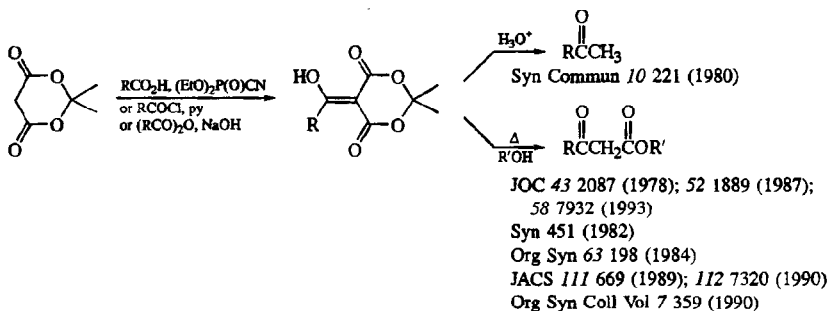
H_2 , cat Pd-C ($\text{R}^2 = \text{PhCH}_2$)

JCS 325 (1950)

H^+

JCS 322 (1950)

JACS 74 831 (1952)



Reagent

$\text{LiCH}_2\text{CO}_2\text{R}$

JACS 111 669 (1989)

JOC 55 386 (1990)

$\text{Me}_3\text{SiO}_2\text{CCH}_2\text{CO}_2\text{R}$, DBU / H_3O^+

TL 35 9323 (1994)

$(\text{RO}_2\text{CCH}_2\text{CO}_2)_2\text{Mg}$

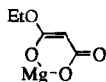
Angew Int 18 72 (1979)

JACS 111 1873 (1989)

TL 30 1345 (1989); 33 4187 (1992)

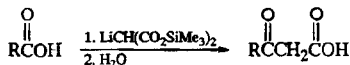
JOC 59 4862 (1994)

SL 105 (1994)

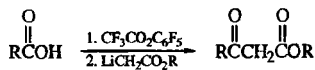


JOC 53 869 (1988); 59 3656 (1994)

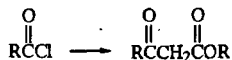
SL 283 (1991)



Syn 787 (1979)



JOC 59 5192 (1994)

 $\text{LiCH}_2\text{CO}_2\text{R}$

See page 1724, Section 2.

 $\text{LiO}_2\text{CCHLiCO}_2\text{R} / \text{H}^+$

JOC 44 310 (1979); 53 3195 (1988)

Chem Pharm Bull 30 2440 (1982)

Org Syn 61 5 (1983)

Org Syn Coll Vol 7 213 (1990)

 $\text{NaCH}(\text{CO}_2\text{R})\text{CO}_2\text{CH}_2\text{Ph} / \text{H}_2$, cat Pd-C or
Pd-BaSO₄

JCS 2758 (1951)

JOC 58 5732 (1993)

 $\text{ROMgCH}(\text{CO}_2\text{R})_2$, Δ

J Prakt Chem 322 (1980)

 $\text{BrMgO}_2\text{CCH}(\text{MgBr})\text{CO}_2\text{R} / \text{H}^+$

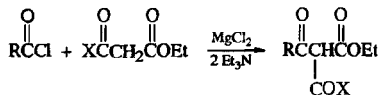
BSCF 945 (1964)

Syn 142 (1978)

JACS 112 7320 (1990)

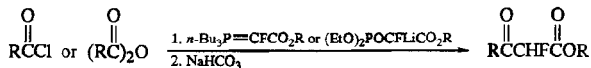
 $\text{Me}_3\text{SiO}_2\text{CCH}_2\text{CO}_2\text{R}$, DBU / H_3O^+

TL 35 9323 (1994)

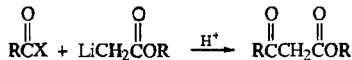


X = Me, OEt

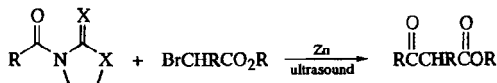
JOC 50 2622 (1987)



JOC 56 273 (1991)

X = OR, Cl, COR, OCO₂R, N(Me)OMe, CN

See page 1724, Section 2.

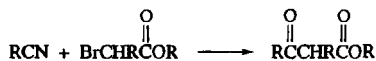


X = O, S

JOC 58 793 (1993)



TL 36 1673 (1995)


 $\text{Zn}/\text{H}_3\text{O}^+$

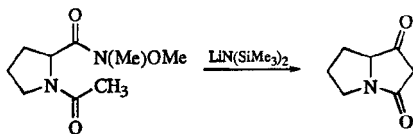
Org Syn Coll Vol 4 120 (1963)

JOC 48 3833 (1983)

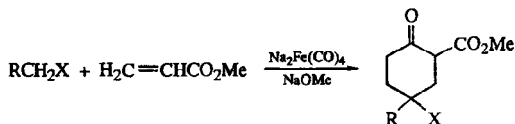
JACS 116 1753 (1994)

 $\text{Zn}, \text{B}(\text{OMe})_3/\text{H}_3\text{O}^+$

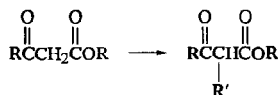
JACS 114 663 (1992)



TL 36 291 (1995)


 $\text{X} = \text{COR}, \text{CO}_2\text{R}, \text{CN}$

JOC 58 4997 (1993)


 $\text{R}'\text{OH}, \text{BF}_3$

JACS 62 2389 (1940); 65 552 (1943)

Org Syn Coll Vol 3 405 (1955)

 $\text{R}'_2\text{O}, \text{BF}_3$

JACS 62 2389 (1940); 65 552 (1943)

 $t\text{-BuBr}, \text{AgClO}_4$

Angew Int 5 1044 (1966)

 $\text{RCH}=\text{CH}_2, \text{MnO}_2 \text{ or } \text{AgO} (\text{R}' = \text{CH}_2\text{CH}_2\text{R})$

Syn 454 (1977)

 $\text{base}/\text{H}_2\text{C}=\text{CH}_2, \text{PdCl}_2, \text{Et}_3\text{N}/\text{H}_2 (\text{R}' = \text{Et})$

JACS 99 7093 (1977); 102 4973 (1980)

 $\text{RCH}=\text{CH}_2, \text{PdCl}_2(\text{PhCN})_2/\text{Et}_3\text{N}/\text{CO}, \text{MeOH}$
 $(\text{R}' = \text{CHRCH}_2\text{CO}_2\text{Me})$

JACS 112 6255 (1990)

 $\text{Cs}_2\text{CO}_3, p\text{-AcOCH}_2\text{C}_6\text{H}_4\text{OAc}$

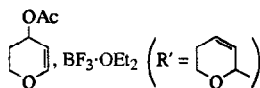
TL 33 5287 (1992)

 $\text{R}_2\text{C}=\text{CHCHROAc}, \text{cat CoCl}_2$

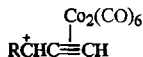
TL 34 6301 (1993)



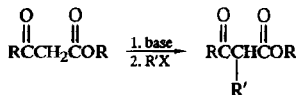
JOC 56 4439 (1991)



CC 68 (1983)



See page 594, Section 8.



Newer Methods Prep Org Chem 2 101 (1963)

Tetr 19 1645 (1963) (rates); 27 4777 (1971) (O vs C alkylation); 33 2737 (1977) (review)

Org Syn 45 7 (1965)

TL 593 (1965) (O vs C alkylation); 3679 (1968) (O vs C alkylation); 4903 (1972) (O vs C alkylation); 23 1993 (1982) (copper enolate); 29 4615 (1988) (surface enhanced chirality); 34 2051 (1993); 35 1759 (1994)

JOC 34 1969 (1969) (O vs C alkylation); 35 171 (1970) (stereochemistry); 48 1362 (1983) (R'X = sulfonium salts); 54 2374 (1989) (R'X = sulfonium salts); 57 4883 (1992); 60 5041 (2-acyl-4-alkanolide), 5107, 7796 (intramolecular) (1995)

Ann 736 1 (1970) (R'X = Me2SO4)

BCSJ 49 1126 (1976) (O vs C alkylation); 52 1716, 3119 (1979)

CC 325 (1980)

Syn Commun 10 279 (1980); 25 1045 (1995)

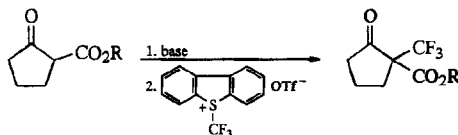
J Chem Res (S) 86 (1982)

Ind J Chem B 21 408 (1982)

JCS Perkin I 2293 (1983) (R'X = allylic halide, regiochemistry)

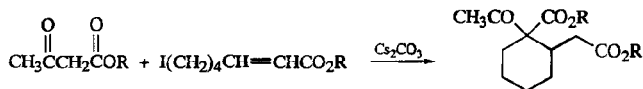
JACS 114 3028 (1992) (pH optimization)

SL 1241 (1995)

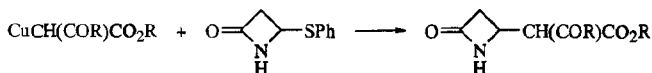


TL 31 3579 (1990)

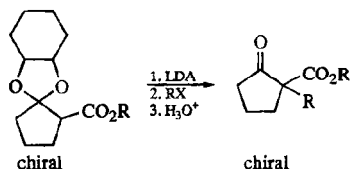
JACS 115 2156 (1993)



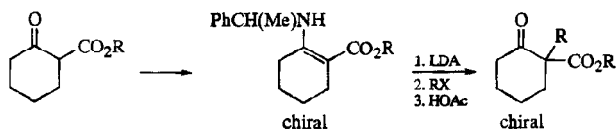
TL 35 2549 (1994)



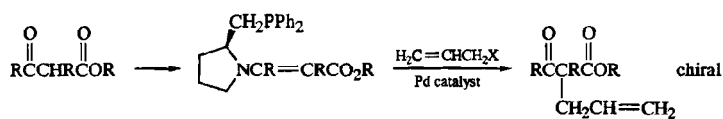
TL 35 5887 (1994)



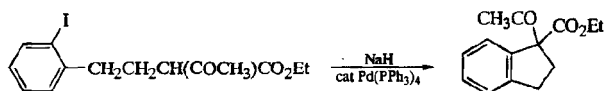
TL 33 247 (1992); 35 1099 (1994)



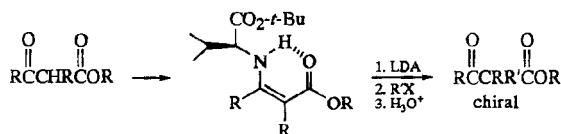
TL 35 1099 (1994)


 X = Br, O₂CR, O₃SAr

TL 31 3623 (1990)

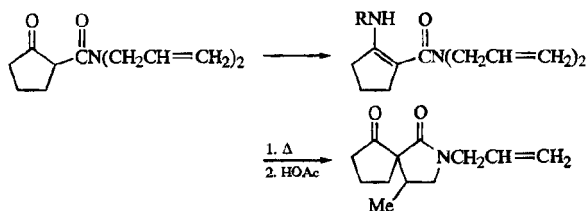


JOC 53 4149 (1988)

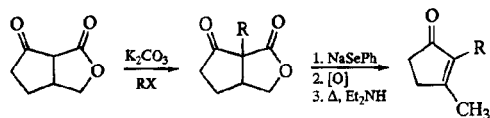


JACS 106 2718 (1984)

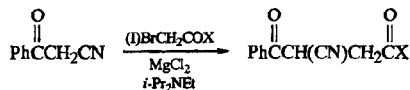
TL 33 17 (1992)



TL 33 4883 (1992)

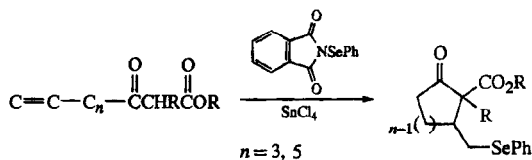


TL 22 2447 (1981)

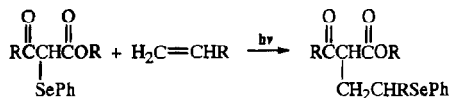


X = R, OR

TL 29 3437 (1988)



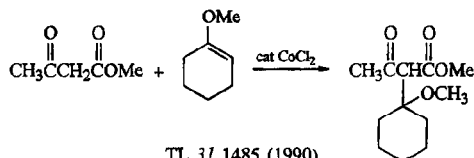
CC 1251, 1252 (1982)



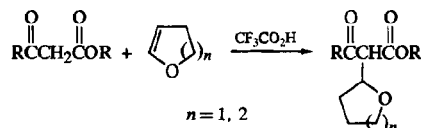
CC 354 (1991) (intramolecular)

TL 33 6953 (1992)

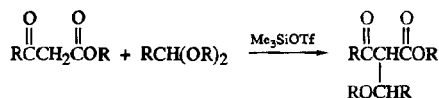
SL 699 (1993) (intramolecular)



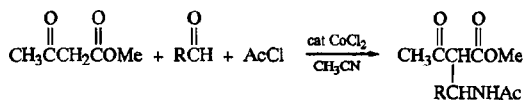
TL 31 1485 (1990)



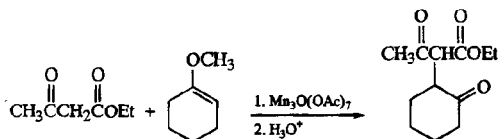
JOC 54 4291 (1989)



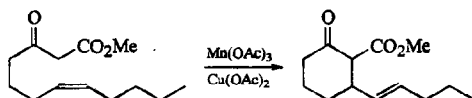
JOC 53 5540 (1988)



TL 36 4877 (1995)



TL 28 175 (1987)

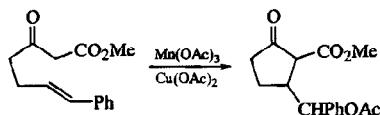


JOC 50 3659 (1985); 55 2427 (1990); 58 7640 (1993) (chiral)

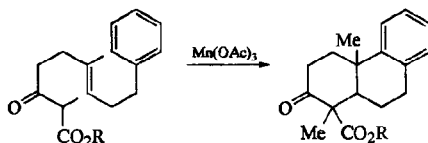
TL 28 845 (1987); 29 5209 (1988); 31 59 (1990)

JACS 113 6607 (1991)

SL 831 (1995)

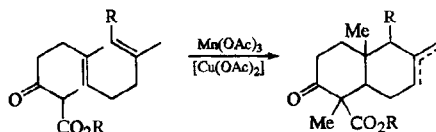


TL 28 6109 (1987)



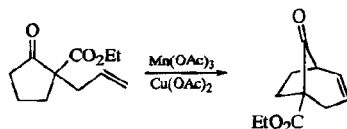
JOC 50 3659 (1985); 57 4195 (1992); 58 7640 (1993) (chiral)

TL 28 845 (1987)

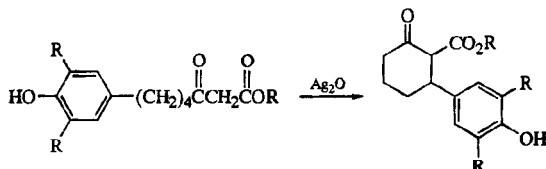


TL 28 841 (1987); 32 4819 (1991); 33 2637, 5921 (1992); 36 2925, 2929 (1995)

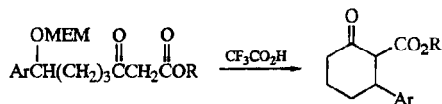
JOC 52 5487 (1987); 58 6217, 7640 (chiral) (1993)



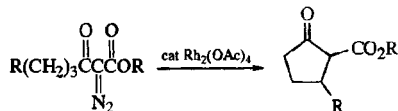
JOC 60 5376 (1995)



JACS 111 1136 (1989)



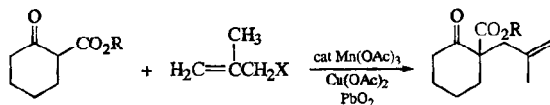
JOC 56 2853 (1991)



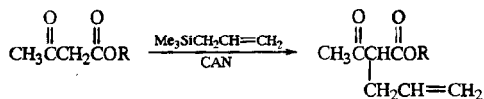
See page 1329, Section 1.



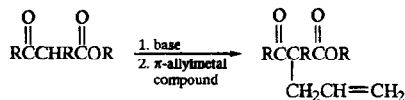
TL 30 4092 (1989)

 $\text{X} = \text{RS}, \text{RSO}_2$

TL 31 357 (1990)

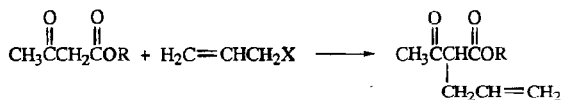
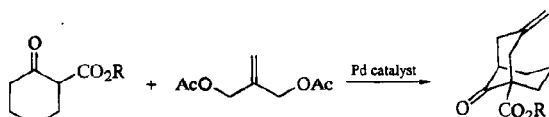


JOC 60 856 (1995)



Metal

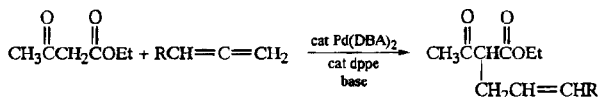
- Mo** JACS 104 5543 (1982); 105 3343 (1983);
 109 1469 (1987); 112 9590 (1990)
 Organomet 2 1687 (1983)
 JOMC 252 105 (1983)
 JOC 55 1127 (1990)
- W** JACS 105 7757 (1983)
- Pd** Tetr 33 2615 (1977) (review)
 J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980) (review)
 Acct Chem Res 13 385 (1980) (review)
 R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985) (review)
 JOC 54 2759 (1989)
 TL 32 2025 (1991); 33 3527, 3531 (both intramolecular), 8001 (1992); 34 6333 (1993); 35 8013 (1994); 36 535 (1995)
 SL 301 (1992)
 JACS 117 5776 (1995)



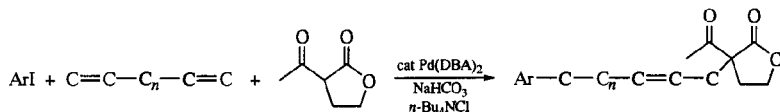
X

Catalyst

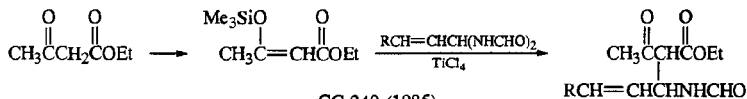
- OH** Co(III) dimethylglyoxime TL 36 6761 (1995)
- OAc** CoCl₂ TL 34 6301 (1993)



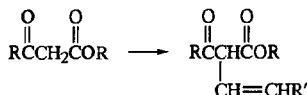
TL 36 3853 (1995)



JOC 56 4589 (1991)



CC 240 (1985)

PhSO₂C≡CSiMe₃, KF, crown ether / Al(Hg)
(R' = H)

JOC 47 4713 (1982)

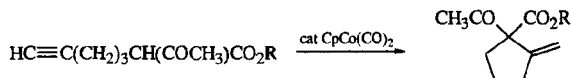
R'CH=CHPb(OAc)₃

CC 965 (1984)

TL 30 7195 (1989)

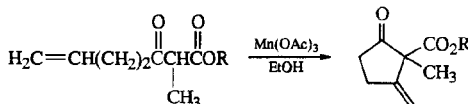
base / H₂C=CH₂, PdCl₂, Et₃N (R' = H)

JACS 99 7093 (1977); 102 4973 (1980)

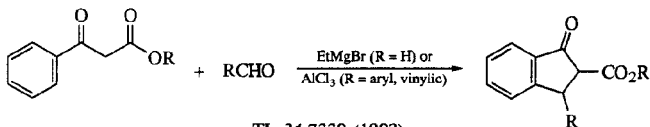


SL 92 (1994)

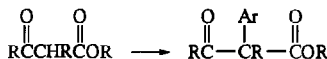
TL 35 6677 (1994)



JOC 56 5544 (1991)



TL 34 7339 (1993)

ArH, PhI(O₂CCF₃)₂

JACS 116 3684 (1994)

ArPb(OAc)₃

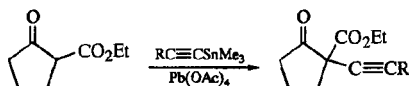
Austral J Chem 33 113 (1980); 38 1155 (1985)
 TL 23 5365 (1982); 31 6637, 7449 (1990); 32 3835,
 5999 (1991); 33 3867 (1992)
 Org Syn Coll Vol 7 229 (1990)
 JOC 60 3052 (1995)

Ph₄BiX (X = O₂CR, O₃SR), *N*-*t*-butyl-*N'*, *N''*-tetramethylguanidine

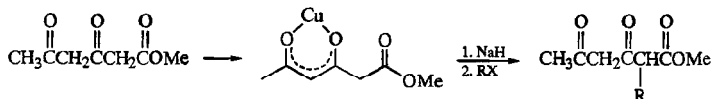
TL 23 3365 (1982)

KO-*t*-Bu / σ -, *m*- and *p*-NC-Ar-Br, NH₃, hv

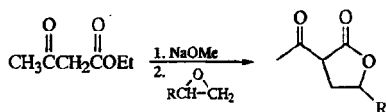
Tetr 38 3479 (1982)



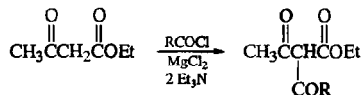
TL 27 5025 (1986)



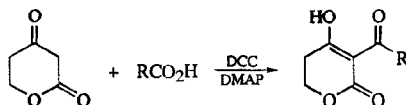
TL 28 3715 (1987)



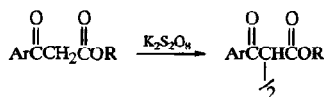
Tetr 40 3471 (1984)



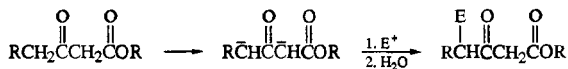
JOC 50 2622 (1985); 60 3074 (1995)



JOC 59 4749 (1994)

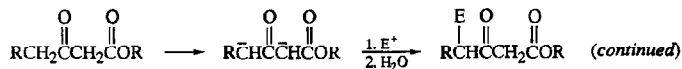


SL 421 (1990)



E⁺
RX

JOC 29 3249 (1964); 38 3428 (1973); 39 2648 (1974); 47 381 (1982); 51 4424 (1986); 52 28, 192 (1987); 57 5058 (1992); 59 6322, 7383 (intramolecular) (1994); 60 7821 (1995)

 E^+

BCSJ 40 2909 (1967)
 Org Rxs 17 155 (1969) (review)
 JACS 92 6702 (1970); 96 1082 (1974); 106 6006
 (1984) (RX = allylic phosphate); 107 196, 2122,
 2712, 5732, 7967 (1985); 108 8235 (1986); 110
 5533, 6210 (1988); 115 6803 (1993)
 Can J Chem 60 673 (1982)
 TL 24 699 (1983); 26 3059 (1985); 27 131, 5555
 (1986); 28 731 (1987); 29 5169 (1988)
 CC 265 (1986)

epoxide

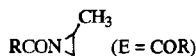
JOC 38 3428 (1973); 43 788 (1978); 54 2183 (1989)
 JACS 100 1938 (1978)
 Heterocycles 10 111 (1978)
 Tetr 35 1601 (1979); 44 6881, 6889 (1988)
 CL 337 (1985)
 TL 28 3597 (1987); 36 523 (1995)
 SL 529 (1992)

RCHO, R₂CO

SL 764 (1993)
 JOC 29 3249 (1964); 47 1779 (1982); 52 4062
 (1987); 58 2523 (1993)
 BCSJ 40 2909 (1967)
 TL 4835 (1971); 27 4713 (1986); 28 5253, 5661
 (1987); 30 4045 (1989)
 CC 362 (1974)
 JACS 104 5528 (1982); 108 2662 (1986); 110 3560
 (1988)
 Ann 1173 (1982)
 JCS Perkin 1 665 (1982)
 SL 837 (1995)

RCO₂R

JOC 29 3249 (1964); 55 1611 (1990)
 TL 2405 (1972); 27 1445, 2401, 3835 (1986); 28
 2017 (1987); 34 513 (1993)
 CC 362 (1974)
 Can J Chem 52 1343 (1974)
 JACS 107 7760 (1985) (4-alkanolide); 110 6180,
 6186 (1988)



TL 35 5073 (1994)

RCONR₂, BF₃·OEt₂

CL 1145 (1985)

RCON(Me)OMe

JACS 110 6172 (1988)
 TL 29 6467 (1988)



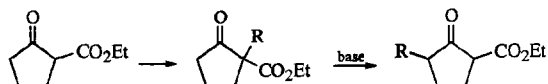
JOC 51 268 (1986)

RCN Can J Chem 52 1343 (1974)

CO₂ JOC 31 1032 (1966)
TL 30 3505 (1989)

NCCO₂R TL 28 1051 (1987)

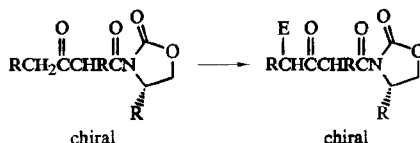
$\text{Ph}_3\text{P}^+\text{CH}=\text{CHCH}=\text{CH}_2/\text{RCHO}$ JACS 112 4991 (1990)
(E = RCH=CHCH=CHCH₂)



Base

NaOEt JOC 29 2781 (1964); 52 28 (1987)
JACS 106 2064 (1984)

KH, 18-crown-6 TL 35 4315 (1994)



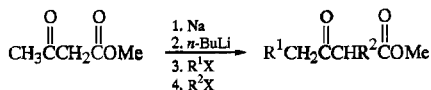
Cy₂BCl, EtNMe₂/RCHO Tetr 48 2127 (1992)
TL 34 2229, 8159 (1993)

SnF₂, N-ethylpiperidine/RCHO JACS 108 2476 (1986)

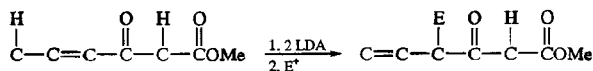
Sn(OTf)₂, Et₃N/RCHO JACS 112 866 (1990)
TL 34 8163 (1993)

TiCl₄, *i*-Pr₂NEt/RCHO JACS 112 866 (1990)

TiCl₄, *i*-Pr₂NEt/ (R = Me, Et) JACS 112 8215 (1990)
TL 34 2229 (1993)

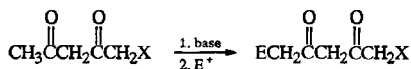


Syn Commun 11 7 (1981)



E⁺ = RX, H₂CO, RCHO, R₂CO

Rec Trav Chim 102 393 (1983)

 X CO_2R E^+

RX

 R_2CO RCO_2R

JOC 46 2566 (1981)

JOC 46 2566 (1981)

CC 362 (1974)

JOC 46 2566 (1981)

JACS 110 6180 (1988)

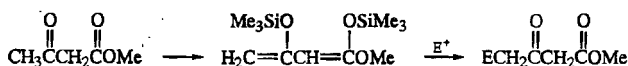
 CONR_2 RX, R_2CO , RCO_2R

JOC 46 2566 (1981)

CN

RX, R_2CO , RCO_2R ,
 $\text{RCON}(\text{Me})\text{OMe}$,
 $\text{RCOCHCO}_2\text{R}$

JACS 110 6180 (1988)

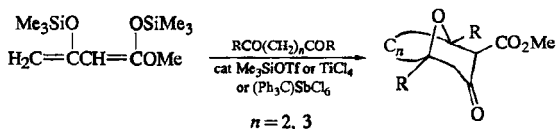
 $\text{E}^+ = \text{Br}_2$, RCHO [TiCl_4 or $\text{TiCl}_2(\text{O}-i\text{-Pr})_2$], $\text{RCH}(\text{OMe})_2$ (TiCl_4), RCOCl

CC 578 (1979); 860 (1986)

Can J Chem 61 688 (1983)

TL 29 3757 (1988)

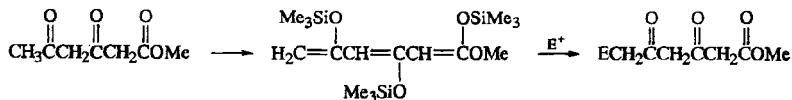
JACS 114 2260 (1992); 115 4497 (1993); 116 3312 (1994)




TL 30 2351 (1989)

JOC 56 2617 (1991); 58 5931 (1993)

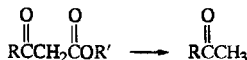
JACS 115 830 (1993)

 E^+ RCHO , TiCl_4

JOC 51 2423 (1986)

 ArCON , TiCl_4 , $\text{Ti}(\text{O}-i\text{-Pr})_4$

JOC 52 2105 (1987) (2-aryl-4,6-dihydroxyarene-carboxylate ester product)

Review: Syn 893 (1982) (H_2O , salts and dipolar aprotic solvents) B_2O_3

TL 3903 (1970)

JOC 38 3436 (1981)

Syn Commun 11 7 (1981)

Al_2O_3 , aq dioxane	TL 2707 (1976)
cat Cs_2CO_3 , $p\text{-H}_2\text{NC}_6\text{H}_4\text{SH}$	JOC 51 3165 (1986)
HBr, HOAc	JOC 54 3761 (1989)
HBr, $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$	JOC 54 3930 (1989)
TsOH	JACS 66 1286 (1944)
H_2SO_4	JACS 75 3152 (1953)
H_2SO_4 , HOAc, H_2O	TL 34 6517 (1993)
$\text{CF}_3\text{CO}_2\text{H} / \Delta$ ($\text{R}' = t\text{-Bu}$)	Syn 996 (1983) JOC 59 1933 (1994)
$n\text{-C}_{17}\text{H}_{35}\text{CO}_2\text{H}$, $(\text{Ph}_4\text{P})\text{Br}$, 170–200 °C	Syn 320 (1985)
H_2O , Δ	JOC 42 459 (1977); 48 2590 (1983)
H_2O , DMSO	TL 1091, 1095 (1974) JOC 43 138 (1978); 52 1880 (1987)
LiCl, H_2O , DMSO	JACS 107 7967 (1985); 108 3435 (1986) CC 265 (1986) TL 28 1725 (1987) JOC 52 1880 (1987)
LiCl, H_2O , DMF	TL 28 5255 (1987)
LiCl, HMPA	CC 1351 (1987)
$\text{LiI} \cdot 2\text{H}_2\text{O}$, 2,4,6-collidine	Org Syn 45 7 (1965) JOC 56 3102 (1991)
$\text{LiI} \cdot 3\text{H}_2\text{O}$, 2,6-lutidine	JACS 107 8066 (1985)
$\text{LiI} \cdot 3\text{H}_2\text{O}$, DMF	JACS 106 6690 (1984)
NaCl, H_2O , DMSO	TL 957 (1973); 28 1439, 3131 (1987) JOC 51 5450 (1986); 52 28 (1987) JACS 109 7477 (1987)
NaCl, H_2O , DMF	JACS 101 7032 (1979)
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, DMSO	Syn 119 (1981) JOC 48 2590 (1983)
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	Heterocycles 16 381 (1981) SL 453 (1990) JOC 59 6922 (1994)
MgCl_2 , DMSO or HMPA	Syn 119 (1981)
MgCl_2 , EtSH, DMSO	Syn 119 (1981)
MgCl_2 , Et_3CSH , DMSO	TL 27 3385 (1986)
Me_3SiI	Syn Commun 9 233 (1979)
NaCN, HMPA	TL 3565 (1973)
DABCO	JOC 39 2647 (1974)

DMAP, H₂O, Δ

TL 26 3059 (1985)

cat DMAP, phosphate buffer

JOC 54 3474 (1989)

W-2 Raney Ni, cat Et₃N (R' = PhCH₂)

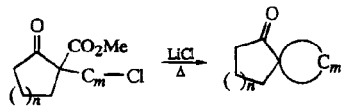
TL 30 7195 (1989)

cat Pd(OAc)₂, cat PPh₃, HCO₂H, Et₃N (R' = allylic)

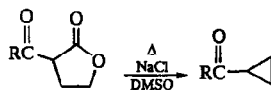
TL 31 3913, 6637 (1990)

~ 500 °C

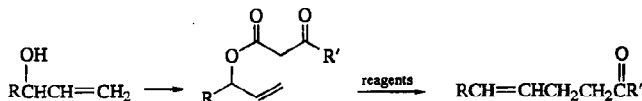
JOC 22 1189 (1957)

 $n, m = 1, 2; 1, 4; 2, 4; 3, 4; 8, 4$

CC 30 (1981)



TL 4389 (1975)



Carroll reaction

Reagents

Δ

JCS 704, 1266 (1940); 507 (1941)

JACS 65 1992 (1943); 102 862 (1980)

JOC 23 153 (1958) (propargylic alcohol); 33 925 (1968); 59 6014 (1994)

TL 3253 (1969); 32 6421 (1991); 34 1149 (1993)

Helv 57 771 (1974)

CC 990 (1976)

Tetr 34 2179 (1978)

Syn Commun 11 237 (1981)

JCS Perkin I 2909 (1982)

alumina

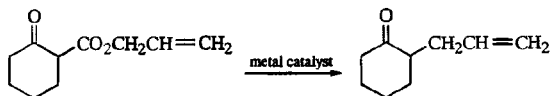
TL 28 4893 (1987)

2 LDA

JOC 49 722 (1984)

Org Syn Coll Vol 8 235 (1993)

SL 209 (1994)



Metal

Mo, Rh, Ni

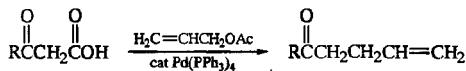
CL 1721 (1984)

Pd

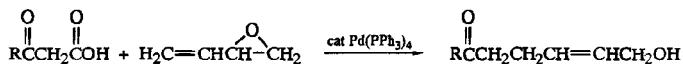
TL 21 3199 (1980); 23 5279 (1982); 26 5575 (1985)

JACS 102 6381 (1980)

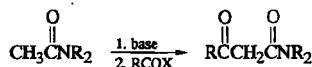
JOC 52 2988 (1987); 54 2726 (1989)



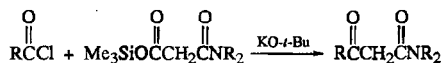
See page 236, Section 8.



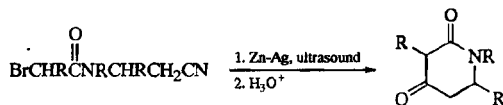
JOC 51 5216 (1986)



See page 1778, Section 4.



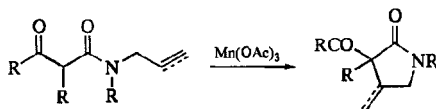
JACS 108 5559 (1986)



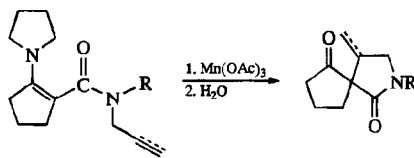
JOC 56 2091 (1991)



JOC USSR 18 1423 (1982)



TL 30 4531 (1989)



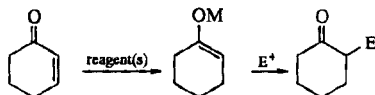
SL 202 (1993)

	$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCX} \end{array} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{RCCH}_2\text{CN} \end{array}$	
<u>X</u>	<u>Reagents</u>	
Cl	LiO ₂ CCHLiCN/H ⁺	JOC 47 5115 (1982); 59 5305 (1994)
	<i>t</i> -BuO ₂ CCH ₂ CN, (EtO) ₂ POCN, Et ₃ N/ <i>p</i> -TsOH, H ₂ O	Syn 308 (1983) JOC 47 5115 (1982)
OR	LiCH ₂ CN	See page 1801, Section 6.
OCO ₂ R	LiCH ₂ CN	See page 1801, Section 6.
N(OMe)Me	LiCH ₂ CN	See page 1801, Section 6.

23. Alkylation of Enones

Review: Org Prep Proc Int 23 219 (1991)

See also page 1201, Section 1; and page 1567, Section 15.



<u>Reagent(s)</u>	<u>E⁺</u>	
Li, NH ₃	RX	JOC 53 2308 (1988); 58 1030 (1993); 59 3902 (1994)
Li, NH ₃ , H ₂ O	RX	Org Syn Coll Vol 6 51 (1988) JACS 111 5761 (1989) JOC 54 3449 (1989)
Li, NH ₃ , MeOH	RX	JOC 56 338 (1991)
Li, NH ₃ , <i>t</i> -BuOH	H ₂ O, RX, RCHO	JACS 87 275 (1965); 89 5464 (1967); 102 1218, 1219 (1980) (both 2-alkene-1,4-diones plus RX) JOC 32 2851 (1967); 35 1881 (1970); 40 146 (1975); 54 3449 (1989) Ann Chim 5 129 (1970)
9-BBN	RCHO	SL 349 (1991)
CB	RCHO	JOC 55 5678 (1990) SL 349 (1991)
(Li)KHB(<i>sec</i> -Bu) ₃	RX	JOC 41 2194 (1976) JACS 107 196 (1985)
<i>t</i> -Bu ₂ AlH, <i>t</i> -BuCu	RCHO	TL 31 5599 (1990)

i-Bu₂AlH, cat MeCu,
HMPA / MeLi

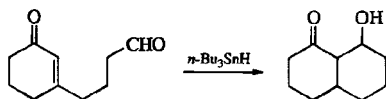
RX

JOC 52 439 (1987); 60 7837
(1995)

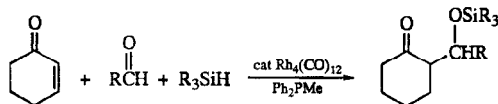
LiHAl(OMe)₃, CuBr

RX

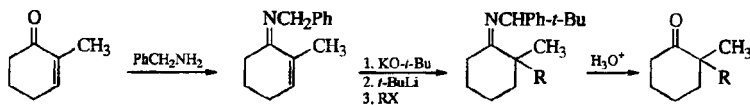
JOC 56 338 (1991)



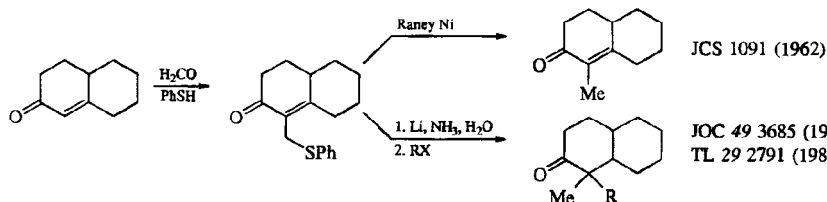
JOC 60 1112 (1995)



TL 31 5331 (1990)

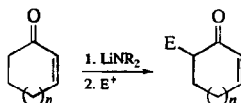


JACS 100 292 (1978)



JCS 1091 (1962)

JOC 49 3685 (1984)
TL 29 2791 (1988)



$n = 0, 1$; $E^+ = \text{RX}, \text{RCHO}, (\text{MeO})_2\text{CO}$

TL 965 (1973); 22 15 (1981); 23 1631 (1982); 27 4461 (1986); 28 3027, 5441 (1987); 30 3327, 7075 (1989)
CC 564 (1973); 1720 (1987)

JOC 38 1775 (1973); 40 862 (1975); 44 2593 (1979); 46 4103, 4643 (1981); 48 2318 (1983) (intramolecular
alkylation); 52 3346 (1987); 54 5919 (1989); 58 1900 (1993)

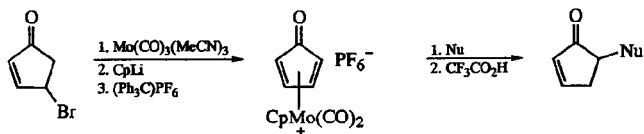
JACS 98 2351 (1976); 106 1443, 3539 (1984); 108 1106 (1986); 111 5312 (1989); 114 7375 (1992)

Syn Commun 7 345 (1977)

Tetr 35 961 (1979)

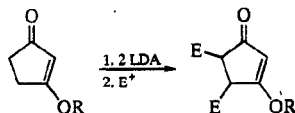
Org Syn Coll Vol 7 208 (1990)

SL 297 (1994) (Mn complexes)



Nu = NaBH_3CN , RLi , RMgX (R = alkyl, aryl, vinylic, alkynyl), ketone enolate, enamine, malonate

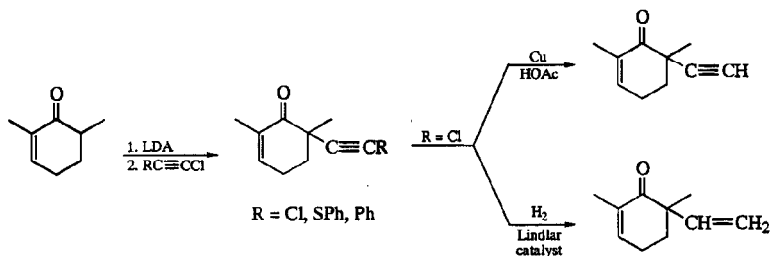
JACS 113 8736 (1991)



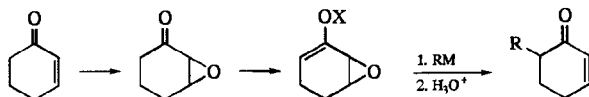
$\text{E}^+ = \text{RX}, \text{RCHO}$

CC 449 (1979)

JACS 105 7203 (1983)



TL 23 2373 (1982)



X

Li

SiMe_3

RM

R_2CuLi (R = Me, Ph)

R_2CuLi (R = Me, Ph)

$(\text{H}_2\text{C}=\text{CH})_2\text{CuMgX}$

$\text{RCu}(\text{CN})\text{Li}$ (R = alkyl, aryl)

JACS 103 2114 (1981)

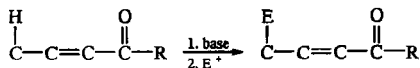
JACS 103 2114 (1981)

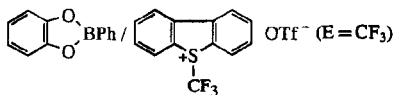
JACS 103 2114 (1981)

JOC 44 4467 (1979); 60 5532 (1995)

CC 1331 (1982)

JACS 104 3165 (1982)



E^+


JOC 59 5692 (1994)

 $RCHO$

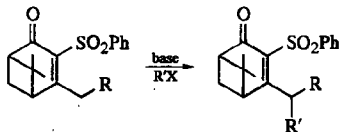
TL 21 711 (1980)

 $RCHO, ZnCl_2$

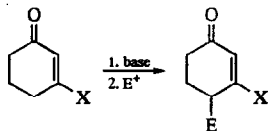
TL 26 4097 (1985)

 $Br_2, PhSO_2Cl$ or $PhSeBr$

TL 4103 (1978)



JOC 58 5145 (1993)


 X

OR

 NR_2
 E^+
 RX
 RX

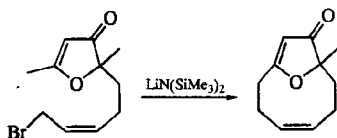
TL 22 15 (1981)

TL 39 (1973); 3963 (1974)

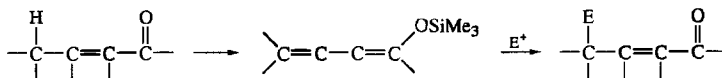
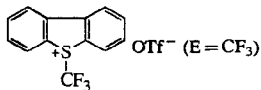
Syn 401 (1976)

JOC 46 4643 (1981)

TL 39 (1973)

 $RCHO, R_2CO$


TL 35 6795 (1994)


 E^+


TL 31 3579 (1990)

JACS 115 2156 (1993)

 $ROCH_2Cl, ZnX_2$

TL 22 705 (1981)

JOC 50 4037 (1985)

pyridinium salt

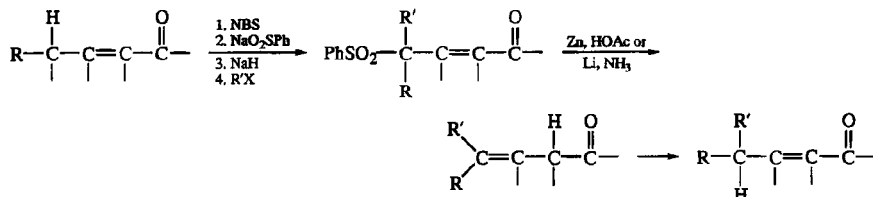
CC 1425 (1983)

PhSCl

TL 3205 (1979)

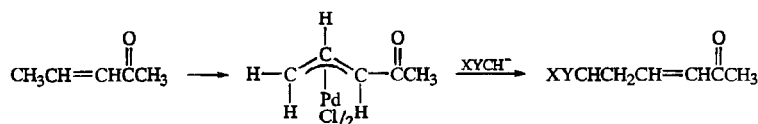


TL 34 721 (1993)



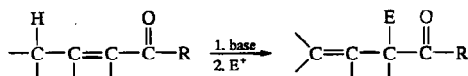
TL 2675 (1978)

IACS 102 1602 (1980)


 X = CO₂R; Y = CO₂R, CN, SO₂R

TL 1589 (1969); 2591 (1975)

Austral J Chem 30 553 (1977)



R

 E⁺

H

RX

alkyl

RX

TL 1273 (1973); 1653 (1974)

JCS 1131 (1957); 4634, 4726 (1963)

IACS 84 284 (1962); 96 7573 (1974); 108 4556 (1986)

Agric Biol Chem 28 95 (1964)

TL 1975 (1967); 459 (1968); 4103 (1978); 26 4097 (1985)

CC 611 (1969); 270 (1980); 75 (1986)

JOC 35 468 (1970); 51 2408 (1986)

CL 55 (1981)

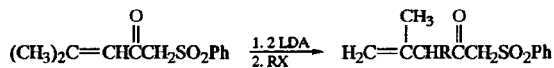
Syn Commun 12 151 (1982)

TL 26 4097 (1985)

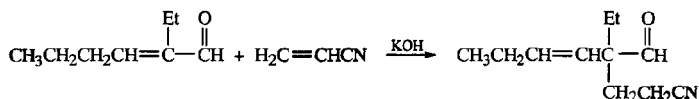
TL 26 4097 (1985)

 RCHO, ZnCl₂

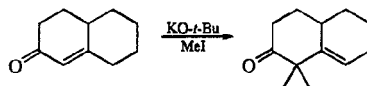
 ROCl or RO₂CCl



TL 27 2725 (1986)



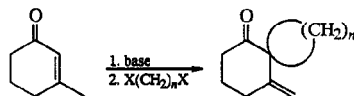
JACS 66 56 (1944)



JACS 76 2852 (1954); 79 5542 (1957); 116 11323 (1994)

JCS 1131 (1957)

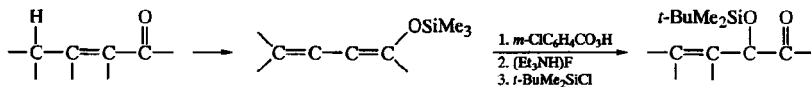
JOC 22 602 (1957); 23 841 (1958); 35 186 (1970)

 $n = 2, 4, 5$

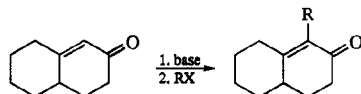
JOC 31 2171 (1966)

JACS 111 2302 (1989); 112 9001 (1990); 115 3056 (1993)

TL 35 2849 (1994)

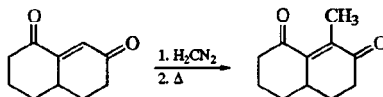


JOC 50 4037 (1985)

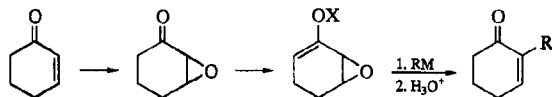


JACS 82 2847 (1960); 108 3841 (1986); 109 3017 (1987)

JOC 32 3008 (1967); 56 713 (1991)



TL 29 4959 (1988)

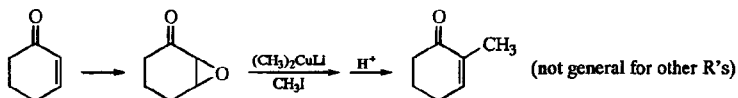

 \underline{X}
 \underline{RM}

Li

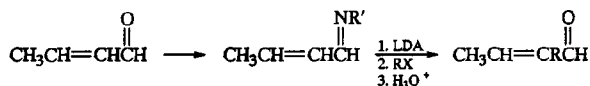
 Ph_2CuLi , PhLi , PhMgBr

JACS 103 2114 (1981)

 SiMe_3
 Ph_2CuLi , $(\text{H}_2\text{C}=\text{CH})_2\text{CuMgBr}$
 Me_2CuLi

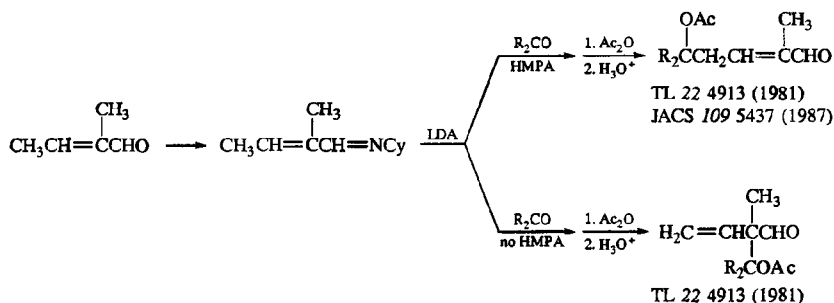
 JACS 103 2114 (1981)
 CC 1331 (1982)


JOC 43 1819 (1978)

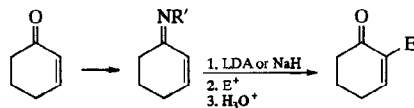

 $\text{R}' = t\text{-Bu, Cy}$

TL 1237 (1975); 597 (1976); 27 4533 (1986)

JACS 115 5466 (1993)



TL 22 4913 (1981)


 $\underline{\text{R}'}$
 $\underline{\text{E}^+}$

Cy

 RX

JACS 93 5938 (1971)

 NMe_2
 RX

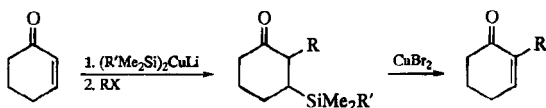
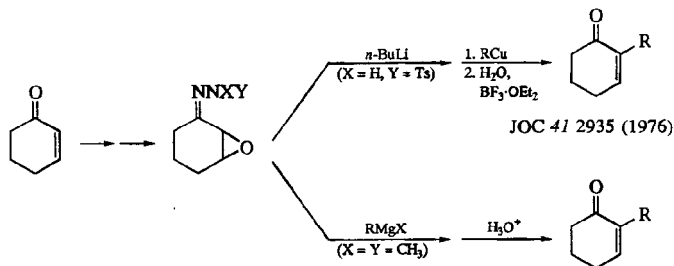
TL 28 3091, 3095 (1987)

Org Syn Coll Vol 6 242 (1988)

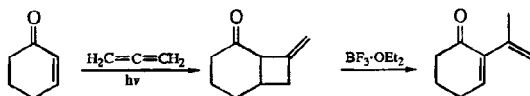
JACS 112 8197 (1990); 114 1438 (1992)

TL 34 3033 (1993)

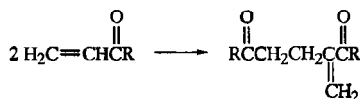
epoxide



JCS Perkin I 2520 (1981)



Syn 139 (1981)

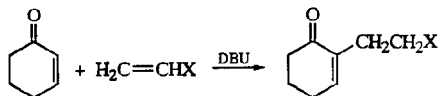


DABCO

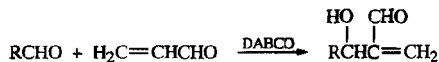
TL 27 4307 (1986); 28 4591 (1987)

DBU

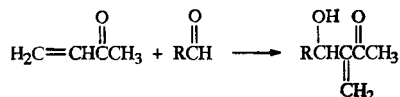
TL 33 6469 (1992)

 $X = \text{CO}_2\text{R}, \text{CN}, \text{SO}_2\text{Ph}$

See page 1809, Section 6.



TL 27 5007 (1986)



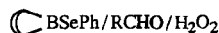
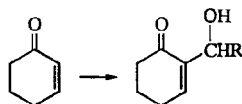
Review: Tetr 44 4053 (1988)

DABCO

TL 27 2031, 4307, 5007 (1986); 31 4509 (1990)

 cat $\text{HRh}(\text{PPh}_3)_4$

CL 1875 (1985)



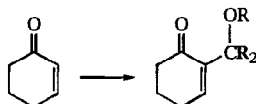
JOC 50 730 (1985)

 Me_2AlX ($\text{X} = \text{SMe}$, SPh or SeMe)/ RCHO / NaIO_4

TL 21 361 (1980)

BCSJ 54 274 (1981)

JACS 109 8017 (1987)


 Me_3SiSePh , cat Me_3SiOTf / $\text{R}_2\text{C}(\text{OR})_2$ / H_2O_2

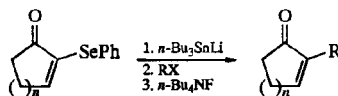
TL 22 1809 (1981)

 Me_3SiOTf , py / $\text{RCH}(\text{OR})_2$ / DBU

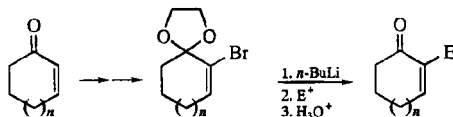
TL 32 2043 (1991)



TL 30 2731 (1989)


 $n = 1, 2$

JOC 57 3145 (1992)


 $n = 0 \text{ or } 1$
 $\text{E}^+ = \text{D}_2\text{O}$, RX , $\text{RCH}=\text{CH}_2$, H_2CO , RCHO , R_2CO , ClCO_2Et , Me_2SiCl , $(\text{MeS})_2$

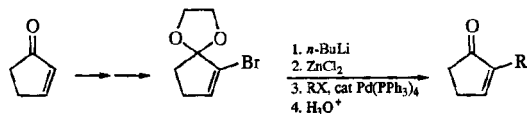
TL 4661 (1978); 31 1977 (1990)

JOC 45 4462 (1980); 47 1855 (1982); 51 1490 (1986)

Syn 389 (1982)

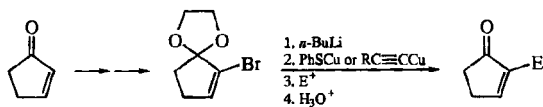
JACS 108 3385 (1986); 112 775, 8465 (1990)

Org Syn Coll Vol 7 271 (1990)

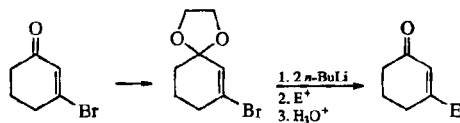


R = aryl, vinylic

CL 1007 (1987)

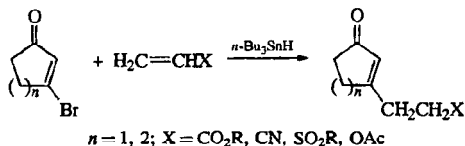
E⁺ = RX (R = alkyl, allylic, benzylic, propargylic), enone (1,4), RO₂CC≡CCO₂R, RCOCl

TL 32 605, 609 (1991)

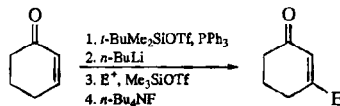
E⁺ = MeI, RCHO, R₂CO, CO₂, Me₃SiCl

TL 22 4217 (1981)

JOC 47 2825 (1982)

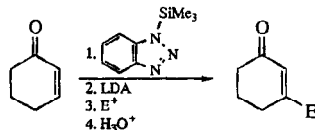


TL 31 4341 (1990)

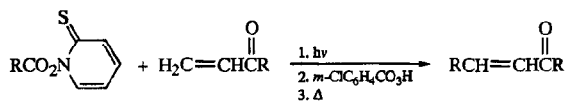
E⁺ = RCHO (no Me₃SiOTf, E = RCH₂), RCHO (E = RCHOH),
H₂C=CHX (X = COR, CO₂R, SO₂R, CN; E = CH₂CH₂X)

JOC 51 3400 (1986)

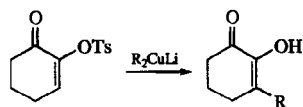
TL 29 5413 (1988)

E⁺ = RX, RCHO, R₂CO, RCO₂R, RNCS

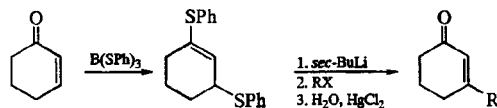
TL 36 5491 (1995)



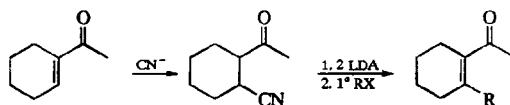
TL 31 1965 (1990)



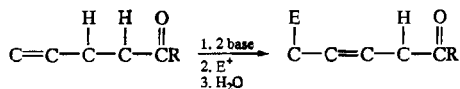
TL 31 315 (1990)



JOC 41 2506 (1976)



TL 3187 (1977)


 $\text{E}^+ = \text{H}_2\text{O}, \text{D}_2\text{O}, \text{RX}, \text{epoxide}, \text{RCHO}, \text{R}_2\text{CO}$

Angew Int 16 320 (1977)

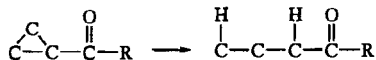
Tetr 37 4047 (1981)

Ann 2272 (1981)

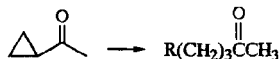
Helv 65 419 (1982)

14. ALKYLATION OF α - AND β -SUBSTITUTED CARBONYL COMPOUNDS

1. Alkylation of Cyclopropyl Ketones



See page 5, Section 1.



Me_3Al , cat $\text{Ni}(\text{acac})_2$

Austral J Chem 28 821 (1975)

R_2CuLi

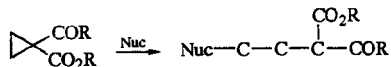
TL 24 4543 (1983)

$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2 \cdot \text{BF}_3$

TL 24 5521 (1983)

$(\text{RCH}=\text{CHCuC}\equiv\text{CC}_3\text{H}_7)\text{Li}$

JCS Perkin I 683 (1983)



Review: *Acet Chem Res* 12 66 (1979)

Nuc

R_2CuLi

TL 529 (1975); 3857 (1976)

Can J Chem 60 825 (1982)

$\text{RCu}(\text{CH}_2\text{SOCH}_3)\text{Li}$, $\text{BF}_3 \cdot \text{OEt}_2$

JOC 52 1885 (1987)

$\text{RCu}(\text{CN})(\text{CH}_2\text{SOCH}_3)\text{Li}_2$

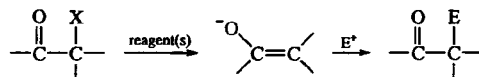
JOC 52 1885 (1987)

$\text{RCu}(\text{CN})(\text{CH}_2\text{SOCH}_3)\text{Li}_2$, $\text{BF}_3 \cdot \text{OEt}_2$

JOC 52 1885 (1987)

Et_2AlCN (Nuc = CN)

Can J Chem 60 825 (1982)

2. Reduction and Alkylation of α -Substituted KetonesXReagent(s)

Br

Li, NH₃

Chem Ind 118 (1963)

Tetr 20 357 (1964)

Zn

JACS 89 5727 (1967)

Ann 459 (1982)

CH₃MgBr

JCS 2933 (1965)

OH, OAc

Li, NH₃

Chem Ind 118 (1963)

Tetr 20 357 (1964)

⁺PPh₃

Na(Hg)

TL 32 4953 (1991)

CN

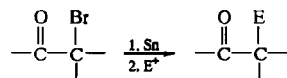
Li, NH₃

JACS 104 2198 (1982)

HgCl

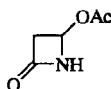
Li, NH₃

JOC 29 1868 (1964)

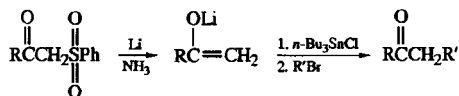
E⁺

RCHO

CL 467 (1982)

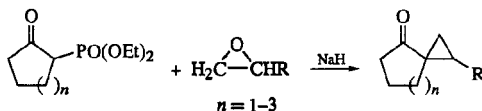


TL 29 61 (1988)



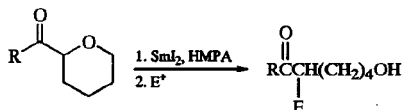
R' = allylic, benzylic, propargylic

JOC 50 3846 (1985)

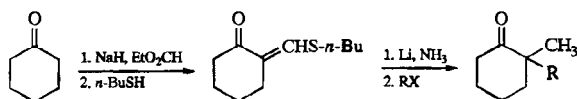
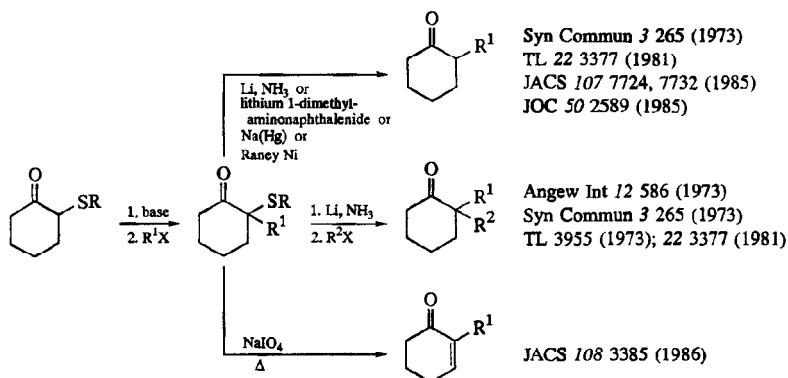


n = 1-3

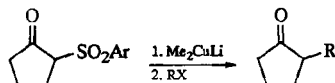
JOC 58 4584 (1993)

E⁺ = H₂O, RX, R₂CO

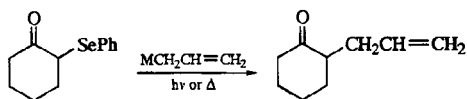
JOC 60 1110 (1995)



JACS 93 1027 (1971); 104 2198 (1982)



JACS 107 1239 (1985)



M

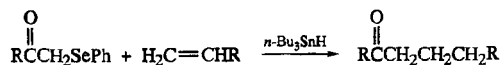
Sn

JACS 110 4815 (1988)

TL 33 4037 (1992)

Pb

TL 33 4037 (1992)



TL 31 227 (1990)



X = H, CO₂R, SO₂Ph

TL 33 6953 (1992)

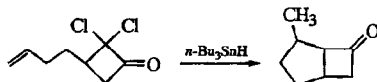


$\text{R}' = \text{alkyl, SiR}_3, \text{OR, SR}$

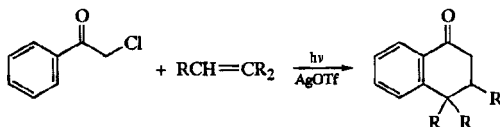
JOC 58 2678 (1993)

3. Substitutive Alkylation of α -Halocarbonyl Compounds

3.1. Free Radical Reactions



JACS 114 10084 (1992)

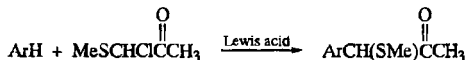


TL 25 1821 (1984)

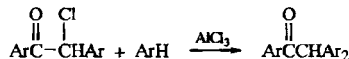
Tetr 48 9687 (1992)

JOC 59 3744 (1994)

3.2. Electrophilic Substitution

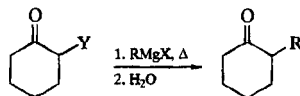


Chem Pharm Bull 30 3574 (1982)



JACS 112 3068 (1990)

3.3. Organolithium and -magnesium Compounds



$\text{Y} = \text{Cl, Br}$

R

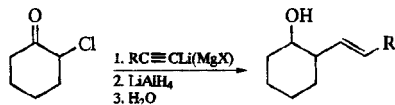
alkyl (low yields)

JACS 56 1990 (1934); 73 1993 (1951)

Compt Rend 198 941 (1934)

JOC 37 4090 (1972)

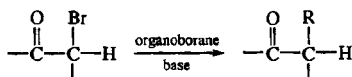
aryl JACS 66 1550 (1944); 70 495 (1948); 71 3313 (1949); 72 1995 (1950)
 JOC 12 737 (1947); 19 1363 (1954); 24 843 (1959)
 vinylic TL 22 2243 (1981)
 Tetr 37 3967 (1981)
 JCS Perkin I 225 (1987)



JACS 105 3348 (1983)
 Org Syn Coll Vol 7 456 (1990)

3.4. Organoboron Compounds

Review: Organomet Chem Syn 1 305 (1972)



Organoborane

R_3B

R-9-BBN

Base

KO-*t*-Bu

KO-*t*-Bu

2,6-(*t*-Bu)₂C₆H₃OK

JACS 90 6218 (1968)

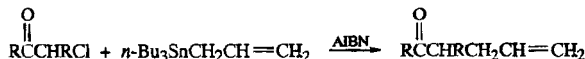
JACS 91 2147, 4304 (1969); 111 1754 (1989)

JACS 91 6852 (1969)

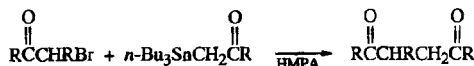
JOC 51 3398 (1986)

(R = vinylic)

3.5. Tin Reagents



CL 795 (1978)



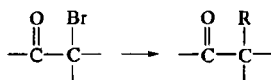
JCS Perkin I 3205 (1990); 859 (1993)

JOC 59 4386 (1994)



JOC 59 486 (1994)

3.6. Organocopper Compounds

 Me_2CuLi

TL 177 (1971)

JOMC 153 259 (1983)

 Ar_2CuLi

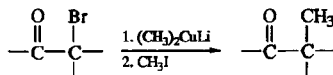
JOC 57 3627 (1992); 60 1856 (1995)

 $(\text{H}_2\text{C}=\text{CMe})_2\text{CuLi}$

J Ind Chem Soc 45 1026 (1968)

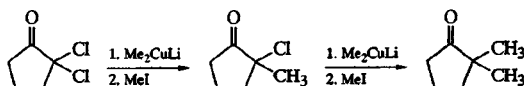
 $\text{MeCu}(\text{CN})\text{Li}$

JOMC 153 259 (1983)



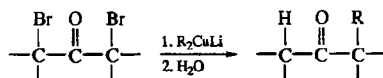
JACS 95 3076, 7788 (1973)

Tetr 31 1223, 1227 (1975)



JOC 45 2036 (1980); 48 4763 (1983)

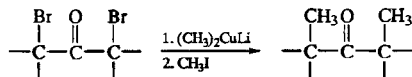
JACS 105 2435 (1983)



JACS 95 3076, 7788 (1973) (both R = Me)

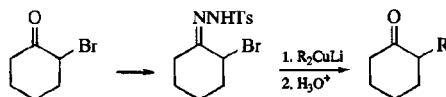
Tetr 31 1223, 1227 (1975) (both R = Me)

TL 27 4671 (1986) (R = Ph)



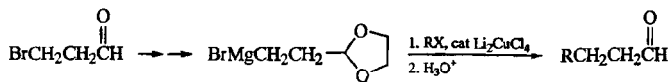
JACS 95 3076, 7788 (1973)

Tetr 31 1223, 1227 (1975)



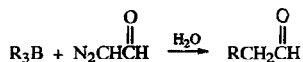
JACS 97 7372 (1975)

4. Substitutive Alkylation of β -Halocarbonyl CompoundsFor the related chemistry of β -halo enones, see page 1546, Section 23.

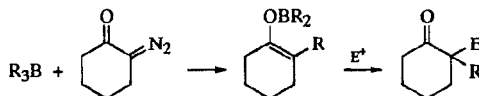


JOC 48 1767 (1983)

5. Substitutive Alkylation of α -Diazocarbonyl Compounds



Can J Chem 48 868 (1970)


 E^+
 H_2O or D_2O

JACS 90 5936 (1968); 91 6195 (1969)

CC 139 (1969)

Can J Chem 49 2371 (1971)

Org Syn Coll Vol 6 919 (1988)

 $2 \text{RLi} / \text{R}'\text{X} \text{ (E = R')}$

JOC 36 1790 (1971)

 $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OLi} / \text{R}'\text{X} \text{ (E = R')}$

Syn Commun 10 139 (1980)

 $(\text{Me}_2\text{N}=\text{CH}_2)\text{I}$

JACS 95 602 (1973)

 $\text{R}'\text{CN} / \text{H}_3\text{O}^+ \text{ (E = COR')}$

Syn Commun 12 189 (1982)

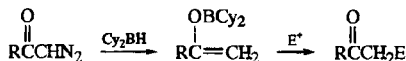
NCS or NBS

Can J Chem 50 2387 (1972)

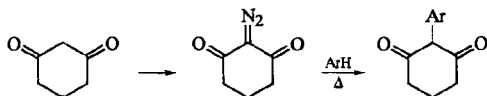
PhSeCl

Syn Commun 10 667 (1980)

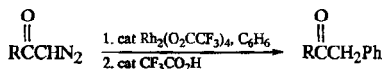
For other reactions of boron enolates, see page 1317, Section 8.


 $\text{E}^+ = (\text{Me}_2\text{N}=\text{CH}_2)\text{I}, \text{RCHO}, \text{R}_2\text{CO}$

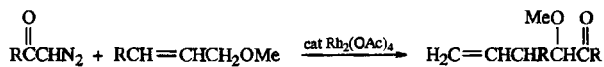
JOC 52 1347 (1987)



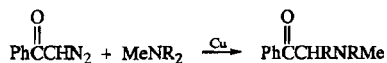
JOC 44 4906 (1979)



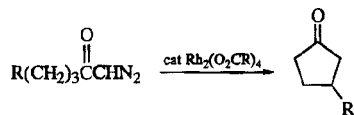
CC 491 (1985)



TL 29 5119 (1988)



Syn 977 (1993)



See page 1329, Section 1.

6. Decarboxylation-Allylation of β -Keto Acids and Esters

See page 1528, Section 22.

15. 1,4-ADDITION TO α,β -UNSATURATED CARBONYL COMPOUNDS AND DERIVATIVES

Reviews:

Org Rxs 38 225 (1990) (β -addition followed by α -functionalization)

P. Perlmutter, "Conjugate Addition Reactions in Organic Synthesis. Tetrahedron Organic Chemistry Series, Volume 9," Pergamon, New York (1992)

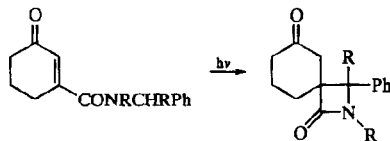
Chem Rev 92 771 (1992) (asymmetric)

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21b, G. Thieme, Stuttgart - New York (1995), pp 2041-2156 (enantioselective)

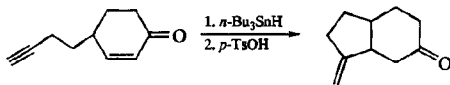
See also page 1455, Section 2; and page 1494, Section 7.2.

1. Free Radical and Related Addition Reactions

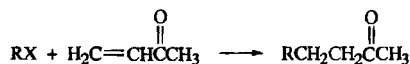
See also page 1615, Section 21.



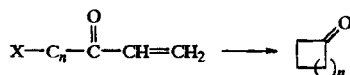
TL 33 1993 (1992)



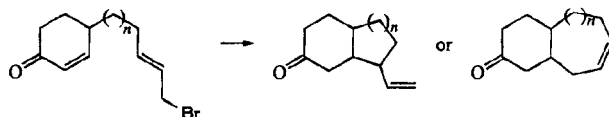
JOC 58 7782 (1993)



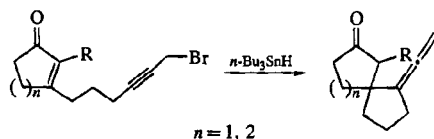
<u>X</u>	<u>Reagent(s)</u>	
Br, I	(Me ₃ Si) ₃ SiH, AIBN <i>n</i> -Bu ₃ SnH	TL 30 681 (1989) TL 28 5853 (1987) (C-glycosides); 29 2335, 5297 (1988); 33 5189 (1992); 34 3087, 6427 (1993); 35 883 (1994); 36 3517 (1995) Ann 427 (1987) JOC 53 1285 (1988); 58 2509 (1993)
	vitamin B ₁₂ , reductant	Pure Appl Chem 55 1791 (1983) (review) Chimia 39 211 (1985) (C-glycosides)
	Zn, cat vitamin B ₁₂ , Et ₃ N	SL 201 (1995)
OCS ₂ Me	<i>n</i> -Bu ₃ SnH	TL 29 351 (1988)



<u>X</u>	<u>Reagent(s)</u>	
Br, I	<i>n</i> -Bu ₃ SnH	JACS 108 2787 (1986); 110 3554 (1988); 111 8309 (1989) JOC 53 93, 3218 (1988); 54 5350 (1989); 55 504, 4883 (1990); 58 1215, 4198 (1993); 59 1396 (1994) TL 30 621, 5989 (1989); 35 2413, 2417, 5161 (1994) JACS 102 3642 (1980)
	vitamin B ₁₂ , reductant	JACS 102 3642 (1980)
OC(S)O- <i>p</i> -Tol	<i>n</i> -Bu ₃ SnH	TL 29 107 (1988) JOC 54 5678 (1989)
SePh	<i>n</i> -Bu ₃ SnH	TL 29 1315 (1988); 30 3865 (1989); 36 417 (1995) JACS 113 9864 (1991)



<i>n</i> -Bu ₃ SnH	JACS 110 6911 (1988)
(Me ₃ Si) ₃ SiH	TL 31 3641 (1990)



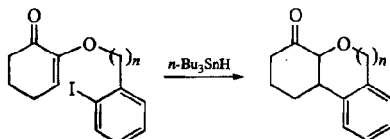
TL 34 5251 (1993)

 $n\text{-Bu}_3\text{SnH}$

TL 24 1871 (1983); 32 4143 (1991); 34 7283 (1993)

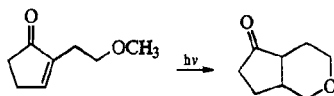
electrolysis, cat Ni(II)

TL 35 725 (1994)

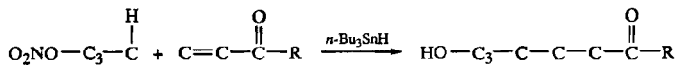
 $n = 0, 1$

TL 34 2879 (1993)

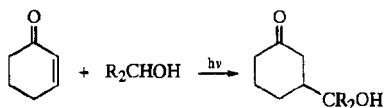
JOC 58 4198 (1993); 59 3933 (1994)



JOC 53 1461 (1988)



JACS 111 6471 (1989)



Compt Rend 255 1817 (1962)

TL 257 (1964); 297, 1957 (1975); 34 7013 (1993)

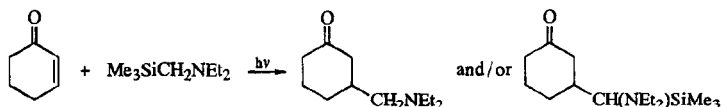
JCS C 2032 (1967)

Can J Chem 46 2535 (1968); 55 3978, 3986 (1977)

JACS 93 5513 (1971)

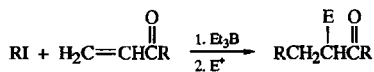
CC 1286 (1972); 319 (1974)

JOC 53 2066 (1988)



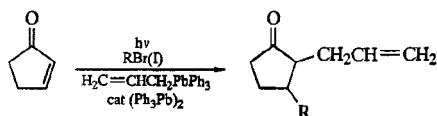
JACS 109 4421 (1987); 110 8099 (1988); 111 406 (1989) (intramolecular); 113 1431, 8847, 8863 (1991) (all intramolecular)

TL 34 5239 (1993); 35 999 (1994) (both intramolecular)

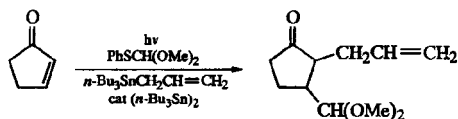


$E^+ = MeOH, RCHO$

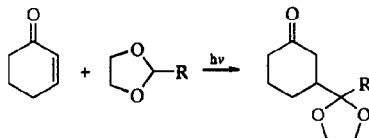
TL 29 1041 (1988)



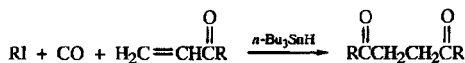
TL 33 4037 (1992)



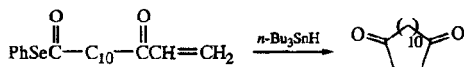
TL 34 6875 (1993)



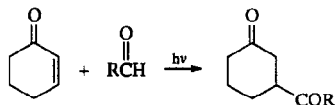
See page 1571, Section 2.



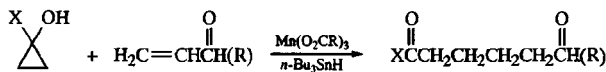
IOC 56 5003 (1991)



SL 335 (1991)



See page 1571, Section 2.



$X = R, OR, NR_2$

BCSJ 66 819 (1993)

2. Michael and Michael-like Addition Reactions

See also page 1616, Section 22.

Reviews of and key references to the Michael reaction:

Org Rxns 10 179 (1959) (review); 47 315 (1995) (intramolecular review)

Syn 107 (1979) (phase transfer)

JOC 44 2239 (1979) (asymmetric); 48 4642 (1983) (annulation)

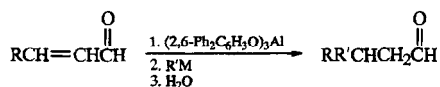
Angew Int 19 1013 (1980) (high pressure); 20 770 (1981) (high pressure, F^- catalyzed)

K. Tomioka and K. Koga in "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Vol 2, Part A, Chpt 7 (asymmetric additions, review)

TL 24 3841 (1983) (high pressure)

Org Prep Proc Int 21 705 (1989) (organolithium reagents)

JACS 116 1571 (1994) (asymmetric La-catalyzed)



R'M

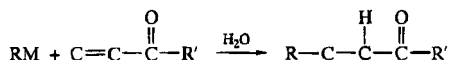
n -BuM (M = Li, MgCl, CaI, SrI, BaI); s -BuMgCl, JACS 116 4131 (1994)

t -BuMgCl, Cl_2CHLi , Br_2CHLi , Cl_3CLi ,

$\text{H}_2\text{C}=\text{CRBaI}$, $\text{RC}\equiv\text{CLi}$, Li ketone and ester enolates

$\text{CF}_3\text{CF}_2\text{Li}$, $\text{F}_2\text{C}=\text{CFLi}$, $\text{C}_6\text{F}_5\text{Li}$

SL 847 (1994)



RM

RLi

JOC 49 1144 (1984)

Helv 68 264 (1985)

TL 28 2525 (1987); 30 127 (1989)

SL 741 (1992)

ArLi

Helv 68 264 (1985)

$\text{RC}\equiv\text{CLi}$

Helv 68 264 (1985)



Helv 68 264 (1985)

RMgX

Helv 68 264 (1985)

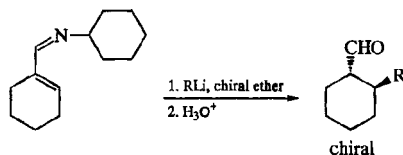
JOC 54 2317 (1989)



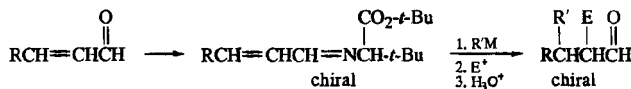
TL 28 3217 (1987)

ArMgX

JOC 54 2317 (1989)



JACS 111 8266 (1989)

 $E^+ = H^+, RX$

Review: K. Tomioka and K. Koga, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1983), Vol 2, Chpt 7

R'M $R'MgX$

JACS 98 7450 (1976); 111 8037 (1989); 112 9292 (1990)

Chem Pharm Bull 27 771 (1979)

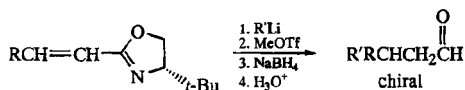
TL 3009 (1979); 21 4005 (1980); 30 2465 (1989)

Tetr 37 3951 (1981)

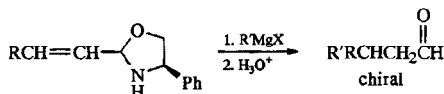
JOC 55 4392 (1990); 57 3615 (1992); 59 5419 (1994)

 $KCH(CO_2Et)_2$

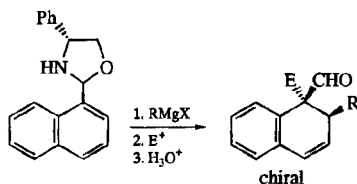
Chem Pharm Bull 27 2437 (1979)



JOC 56 7098 (1991)

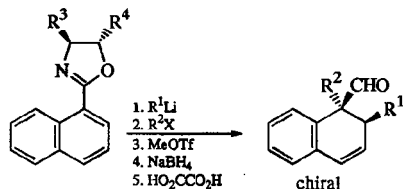


JOC 57 1237 (1992)

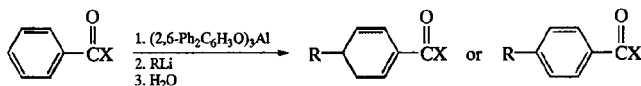
 $E^+ = H^+, RX, ClCO_2R$

JOC 57 1237 (1992)

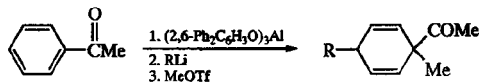
TL 35 4267, 8969 (1994)



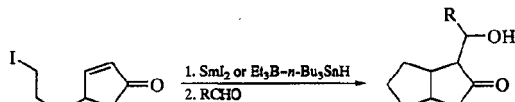
JOC 56 2292, 2607 (1991)

 $X = H, Me; R = 1^\circ, 2^\circ, 3^\circ$ alkyl

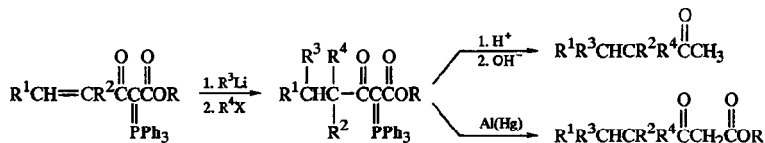
JACS 117 9091 (1995)



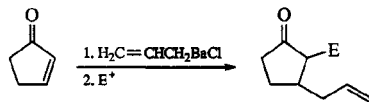
JACS 117 9091 (1995)



SL 317 (1991)



JOC 47 4955, 4963 (1982); 52 1381 (1987) (intramolecular)

 $E^+ = H^+, R_2C=CHCH_2Br, RC\equiv CCH_2Br, RCHO, RCOCl$ (also enol ester formed)

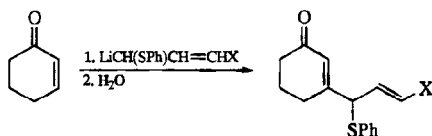
JACS 116 6130 (1994)



JOC 60 4690 (1995)



TL 23 719 (1982)

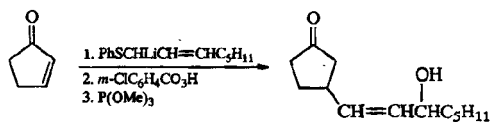
 X

OMe

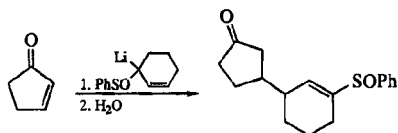
JOC 60 3936 (1995)

SPh

JOC 54 1290 (1989)



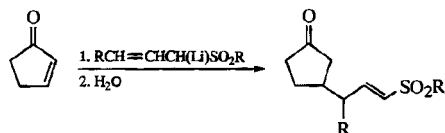
BCSJ 55 3043 (1982)



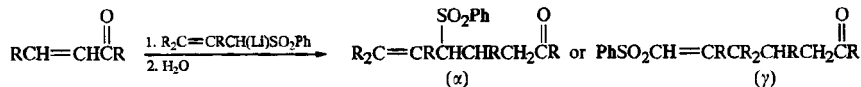
JACS 107 4088 (1985); 108 3835 (1986); 110 5411, 5423 (1988)

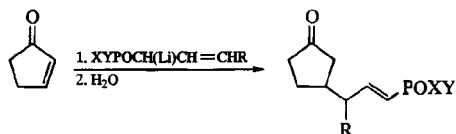
JOC 52 719 (1987); 53 507 (1988)

TL 31 5409 (1990)



JOC 54 1960 (1989)

Syn Commun 8 483 (1978) (α and γ)TL 22 1905 (1981) (α)

X

Ph

Y

Ph

JACS 110 5411, 5423 (1988)

JOC 54 5162 (1989)

TL 36 6309 (1995)

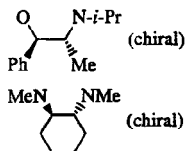
EtO

EtO

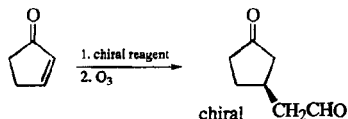
JACS 110 5411 (1988); 113

7424 (1991)

SL 817 (1992)



JOC 58 5032 (1993)

Chiral reagent $\text{R}_2\text{N(RO)POCH(Li)CH=CHR}$

JACS 109 5026 (1987)

JOC 60 7535 (1995)

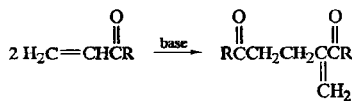
 $(\text{ArO})_2\text{POCH(Li)CH=CHR}$

JOC 60 8036 (1995)

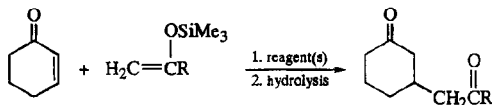


CC 122 (1981)

Tetr 39 117, 999 (1983)



See page 1546, Section 23.

Reagent(s)

montmorillonite clay

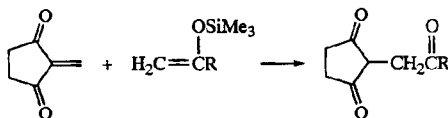
CC 1203 (1987)

BCSJ 61 2157 (1988)

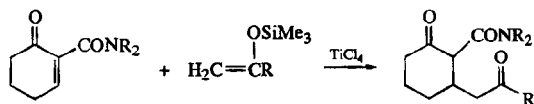
cat $(\text{Ph}_3\text{C})\text{ClO}_4$	CL 953 (1985); 1017 (1986) TL 31 7273 (1990)
cat Ph_3CCl , cat SnCl_2	CL 491 (1987)
CsF	JOMC 184 157 (1980)
$\text{BF}_3 \cdot \text{OEt}_2$, ROH	TL 26 6201 (1985) (also methyl enol ethers used); 34 3863 (1993)
cat $(\text{C}_6\text{F}_5)_3\text{B}$	SL 577 (1993)
cat Me_3SiCl , cat SnCl_2	CL 463 (1987)
SnCl_4	JACS 107 2797 (1985)
cat $n\text{-Bu}_2\text{Sn}(\text{OTf})_2$	TL 31 1581 (1990) Tetr 47 9773 (1991)
cat BiCl_3	TL 29 4719 (1988) BCSJ 64 990 (1991)
cat BiCl_3 , cat NaI or ZnI_2	JOC 58 1835 (1993)
cat $\text{Sc}(\text{OTf})_3$	SL 472 (1993)
TiCl_4	CL 1223 (1974) JOC 45 607 (1980); 50 2539, 4266 (1985); 51 279 (1986) JACS 107 2797 (1985) Org Syn 65 12 (1987) Org Syn Coll Vol 8 210 (1993)
TiCl_4 , $\text{Ti}(\text{O-}i\text{-Pr})_4$	CL 1223 (1974) BCSJ 49 779 (1976) JOC 43 2720 (1978); 50 4266 (1985)
ZnCl_2 -alumina	TL 34 1989 (1993)
cat $\text{Yb}(\text{OTf})_3$	TL 33 6815 (1992)



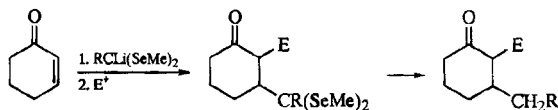
JOC 58 2647 (1993)



JOC 53 4038 (1988)

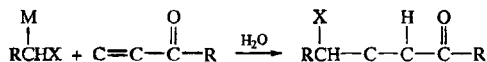


TL 33 4397 (1992)



R = H, Me; $E^+ = H^+, MeI$

TL 22 1623 (1981)



M = alkali metal

\underline{X}

COR

BSCF 3543 (1966)

JCS Perkin I 1879 (1974)

JOC 42 183 (1977); 55 157 (1990); 60 692 (1995)

Tetr 40 4127 (1984); 48 5597 (1992)

TL 27 6169 (1986)

JACS 111 8284 (1989)

CO₂R

JOC 41 4044 (1976); 47 3464 (1982); 50 3022

(1985); 55 157 (1990); 60 6700 (1995)

J Polym Sci, Polym Chem Ed 17 3509 (1979)

TL 27 3927 (1986) (intramolecular)

CS₂Me

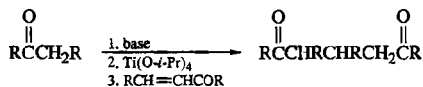
TL 27 1505 (1986)

CONR₂

JOC 50 3019 (1985); 55 132 (1990)

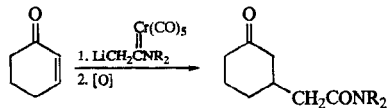
CSNR₂

JOC 55 132 (1990)

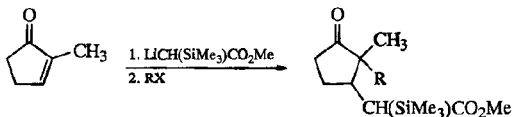


Tetr 48 5597 (1992)

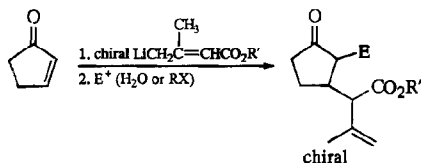
JOC 59 3690 (1994)



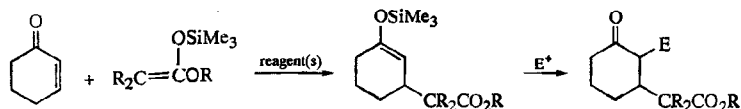
JACS 115 4602 (1993)



SL 249 (1995)



TL 24 4975 (1983)


 $E^+ = H_3O^+; PhSCHClR; ZnBr_2; RX; [(Me_2N)_3S]Me_3SiF_2; RCHO; NBS; PhSeCl$
Reagent(s)

high pressure

TL 24 4943 (1983); 25 1075 (1984)

JOC 49 3264 (1984)

 CH_3NO_2

JOC 49 2083 (1984)

 Δ, CH_3CN

TL 21 3779 (1980); 35 233 (1994)

JCS Perkin I 1099 (1982)

silica gel

TL 29 5241 (1988) (intramolecular)

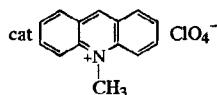
montmorillonite clay

CC 1203 (1987)

cat $LiClO_4$

TL 32 4665 (1991); 34 1119 (1993)

JOC 60 6670 (1995)



TL 32 2405 (1991)

cat $(Ph_3C)ClO_4$

CL 1805, 1817 (1986)

 $(Ph_3C)SbCl_6$

TL 29 1371 (1988)

cat $(C_6F_5)_3B$

SL 577 (1993)

cat $[(Me_2N)_3S]Me_3SiF_2$

JOC 49 2083 (1984)

cat Me_3SiCl, CH_3NO_2

JOC 49 2083 (1984)

cat Et_3SiClO_4

JACS 113 4028 (1991)

cat $Me_3SiCl, cat SnCl_2$

CL 463 (1987)

cat $SnCl_4$

JACS 113 4028 (1991)

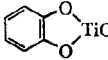
cat $n-Bu_2Sn(OTf)_2$

Tetr 47 9773 (1991)

JACS 113 4028 (1991)

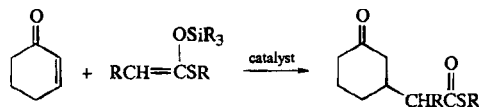
cat $Se(OTf)_3$

SL 472 (1993)

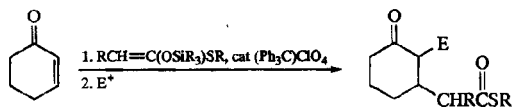
TiCl_4	CL 163 (1976) JACS 102 4262 (1980); 107 2797 (1985); 113 4028 (1991) JOC 45 237 (1980); 51 279 (1986); 57 5054 (1992) JOMC 321 307 (1987) TL 29 5241 (1988) (intramolecular)
TiCl_4 , $\text{Ti}(\text{O}-i\text{-Pr})_4$	CL 163 (1976)
cat 	CL 1171 (1989)
cat $\text{LiCo}(\text{B}_9\text{C}_2\text{H}_{11})_2$	JOC 59 6898 (1994)
ZnI_2	JACS 109 4390 (1987)
HgI_2	JACS 111 2599, 3456 (1989) JOC 54 3738, 6016 (1989); 56 387 (1991)
cat $\text{Yb}(\text{OTf})_3$	TL 33 6815 (1992)
cat SmI_2	TL 34 3881 (1993)
cat P_4O_{10}	TL 35 233 (1994)
various promoters	TL 36 95 (1995)



LiClO_4	TL 32 4665 (1991) JACS 115 5841 (1993)
$\text{TiCl}_2(\text{O}-i\text{-Pr})_2$, chiral diol (enantioselective)	TL 36 1363 (1995)

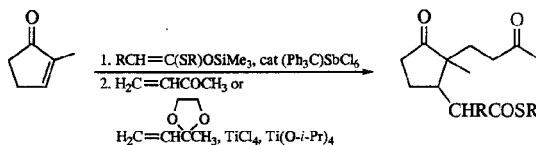
**Catalyst**

SnCl_2 , Ph_3CCl	CL 491 (1987)
$(\text{Ph}_3\text{C})\text{SbCl}_6$	CL 743 (1987) TL 36 5425 (1995)
$\text{Sc}(\text{OTf})_3$	SL 472 (1993)

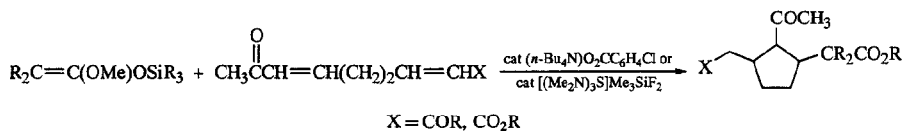


$\text{E}^+ = \text{H}^+$, $\text{HC}(\text{OMe})_3$, RCHO

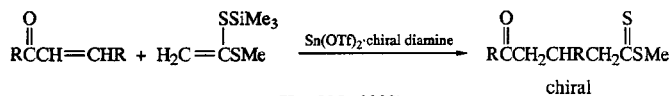
CL 1817 (1986); 743 (1987)
JACS 114 8349 (1992)



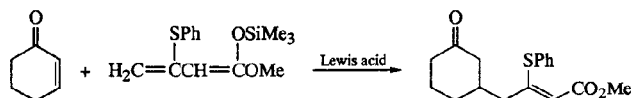
TL 36 5425 (1995)



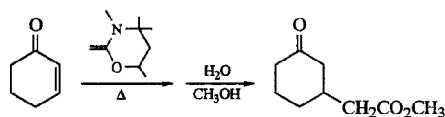
JOC 57 1733 (1992)



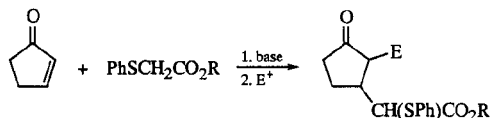
CL 1025 (1988)



JOC 52 110 (1987)

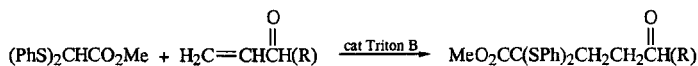


JOC 38 175 (1973)

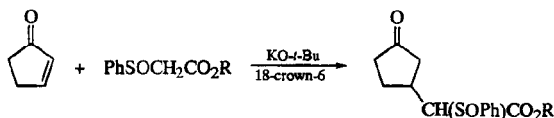
 $\text{E}^+ = \text{H}, \text{RX}$

TL 29 6943 (1988)

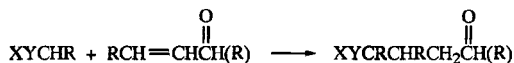
JOC 55 2132 (1990)



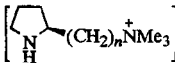
BSCF II 241 (1982)

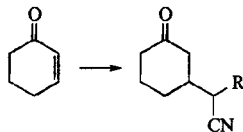


JOC 56 723 (1991)



Review: Org Rxs 10 179 (1959)

<u>X</u>	<u>Y</u>	<u>Reagent</u>	
CHO	COR	KOH	Syn 796 (1983)
CHO	CO ₂ R	K ₂ CO ₃	JOC 54 3831 (1989)
COR	COR	cat LiI alumina NiBr ₂ -clay, FeCl ₃ cat EuCl ₃ cat Eu(tfc) ₃	TL 32 5373 (1991) TL 32 2811 (1991) TL 31 4867 (1990) TL 34 7649 (1993) TL 34 7649 (1993)
COR	CO ₂ R	cat chiral amine alumina cat LiI cat Cu _n (acac) _n (n = 1, 2) cat EuCl ₃ cat Eu(tfc) ₃	JOC 53 1157 (1988) TL 32 2811 (1991) TL 32 5373 (1991) TL 27 5015 (1986) TL 34 7649 (1993) TL 34 7649 (1993)
CO ₂ R	CO ₂ R	alumina KOH, R ₄ NX cat  OH ⁻ (n = 1, 2; chiral) NaOEt	TL 32 2811 (1991) TL 30 333 (1989) TL 35 8805 (1994) Org Syn Coll Vol 8 467 (1993)
CO ₂ R	-CN	La-Na-BINOL (chiral)	JACS 117 6194 (1995)
CO ₂ R	-CN	alumina cat RuH ₂ (PPh ₃) ₄ cat RhH(CO)(PPh ₃) ₃ , chiral bis(phosphine)	TL 32 2811 (1991) JACS 111 5954 (1989) JACS 114 8295 (1992) Tetr 50 4439 (1994)
CO ₂ R	-NC	cat n-Bu ₄ NF	TL 30 1257 (1989)
COSR	COSR	DABCO	Can J Chem 60 94 (1982)
CON(Me)OMe	CN	cat Rh(acac)(CO) ₂ , cat chiral bis(phosphine)	TL 36 6479 (1995)
CN	CN	base	TL 32 5375 (1991)



RCH_2CN ($\text{R} = \text{Ph}, \text{CN}$), cat $\text{RhH}(\text{CO})(\text{PPh}_3)_3$

TL 32 2807 (1991)

$\text{Me}_3\text{SiCHLiCN}$

TL 25 1599 (1984)

JACS 115 4377 (1993); 116 4689 (1994)

ArCHLiCN

Syn Commun 11 85, 335 (1981)

TL 1543 (1979); 22 2171 (1981); 35 3935 (1994)

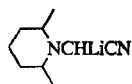
$\text{RCLi}(\text{SPh})\text{CN}$

TL 1121 (1979)

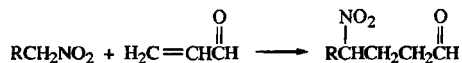
JOC 47 1131 (1982)

$\text{RCLi}(\text{SePh})\text{CN}$

JACS 99 5210 (1977)



Heterocycles 19 1395 (1982)



alumina

Syn 237, 1024 (1986)

cat $n\text{-Bu}_4\text{NF}$

TL 23 3521 (1982)

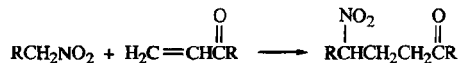
cat Et_3N

TL 23 3521 (1982)

JOC 50 3692 (1985)

cat Ph_3P

TL 23 3521 (1982)



electrolysis

TL 34 4465 (1993)

alumina

Syn 237 (1986)

H_2O

TL 33 8073 (1992)

Amberlyst A-21

JOC 55 5766 (1990)

cat chiral amine

CC 238 (1978)

JOC 53 1157 (1988)

cat chiral amine, pressure

CL 1673 (1981)

cat tetramethylguanidine

TL 23 2957 (1982)

JOC 50 3692 (1985); 53 1871 (1988)

tetramethylguanidine


JOC 50 3692 (1985)

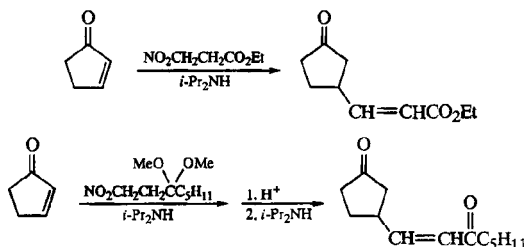
cat $i\text{-Pr}_2\text{NH}$

Org Syn Coll Vol 6 648 (1988)

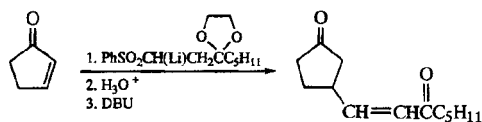
DBU

JOC 50 3692 (1985); 54 4034 (1989)
(intramolecular)

cat <i>n</i> -Bu ₃ P	TL 32 5543 (1991)
KF	TL 29 4189 (1988)
KF, ion exchange resin	JOC 54 4993 (1989)
cat KF, cat 18-crown-6	CC 635 (1982) TL 32 1085 (1991)
cat KF-alumina	BCSJ 56 1885 (1983) JOC 52 1601 (1987)
KF, cat chiral R ₄ NX	JCS Perkin I 547 (1981)
KF, <i>n</i> -Bu ₄ NCl	JOC 55 511 (1990)
cat R ₄ NF	CC 238 (1978)
cat  CO ₂ Rb (chiral)	TL 35 8233 (1994)



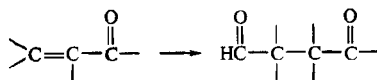
TL 2371 (1978)



CL 607 (1982)



Can J Chem 60 94 (1982)

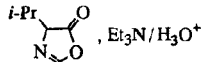
LiC(SPh)₃/CrCl₂, H₂O/hydrolysis

TL 3533 (1978)

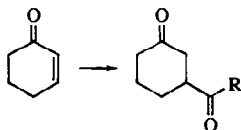
ArSCHLiSOAr/I₂, KI/hydrolysisJCS Perkin I 1284 (1981)
Syn 74 (1981)

TsCHLiSCH₃/H₂O, hv

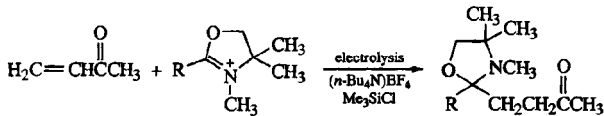
JOC 51 508 (1986)



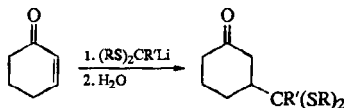
TL 34 3907 (1993)



See subsequent sections on organometallic compounds and page 1435, Section 9.



TL 28 4411 (1987)



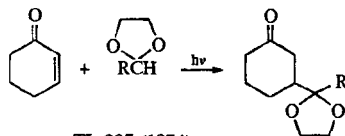
CC 100 (1979); 421 (1982)

Helv 65 385 (1982)

Tetr 38 3285 (1982)

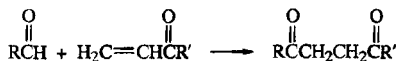
TL 29 3599 (1988)

JOC 54 1290 (1989) (R' = SiMe₃); 55 4340 (1990); 60 4822 (1995)



TL 297 (1974)

Can J Chem 55 3986 (1977)



Reviews:

Angew Int 15 639 (1976)

Org Rxs 40 407 (1991)

See page 1809, Section 6 for analogous conjugate additions to α,β -unsaturated, esters and nitriles.

Reagent(s)

hv (R = alkyl, aryl, vinylic)

Syn Commun 6 417 (1976)

Can J Chem 55 3986 (1977)

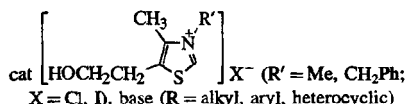
TL 31 3063 (1990); 35 7723 (1994)

cat NaCN (R = aryl, heterocyclic)

TL 1461 (1973)

Angew Int 12 81 (1973)

Ber 107 2453 (1974); 109 534 (1976)



TL 4505 (1974)

Angew Int 13 539 (1974)

Syn 379 (1975); 129, 626 (1981)

Ber 109 2890, 3426 (1976); 112 84, 1410, 2419 (1979); 113 979, 1890 (1980); 114 564, 581, 2479 (1981)

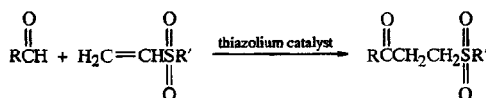
Heterocycles 12 369 (1979)

Ann 1550 (1981)

JOC 51 2712 (1986); 52 2213 (1987); 58 5479 (1993)

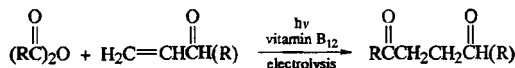
Org Syn 65 26 (1987)

Org Syn Coll Vol 8 620 (1993)

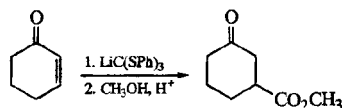
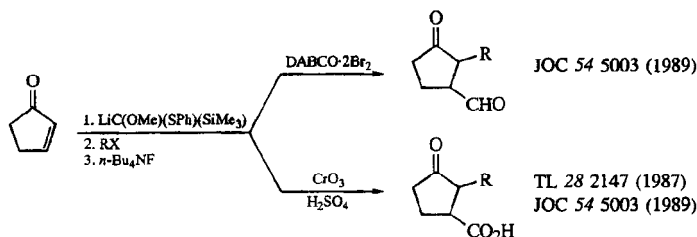


Angew Int 17 131 (1978)

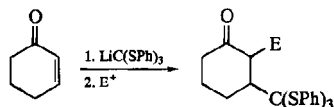
Ber 114 1226 (1981)



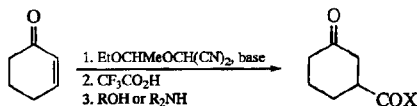
JACS 105 7200 (1983)



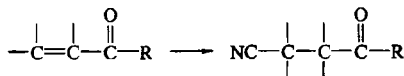
CC 216 (1975)

 $\text{E}^+ = \text{RX}, \text{H}_2\text{CO}$

JOC 55 2132 (1990); 57 1968 (1992)



JOC 56 7195 (1991)



HCN·py (R = alkyl)

JOC 51 902 (1986)

LiCN

TL 28 4189 (1987)

NaCN, NH₄Cl

TL 28 3061 (1987)

KCN

TL 28 2537 (1987)

KCN, NH₄Cl

SL 43 (1993)

t-BuNC, TiCl₄ (R = alkyl)

JACS 104 6449 (1982)

t-BuNC, EtAlCl₂ (R = H)

JACS 104 6449 (1982)

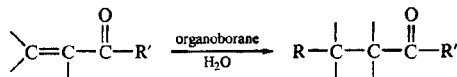
NCCO₂Me, KOAc, Et₃N

SL 833 (1991)

See also page 1589, Section 4.

3. Organoboron Compounds

Review: Angew Int 11 692 (1972)



R'

Organoborane

H

R₃BJACS 89 5709 (1967); 90 4165 (1968);
92 710, 712, 714 (1970)

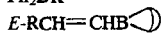
H, alkyl

NaBPh₄, cat Pd(OAc)₂, cat SbCl₃,
NaOAc, HOAcTL 35 1739 (1994)
JOC 60 883 (1995)

alkyl, aryl

R₃BJACS 89 5708 (1967); 90 4166 (1968);
92 712, 714 (1970)
Carbohydr Res 58 39 (1977)
JACS 93 3777 (1971); 95 6757 (1973)Ph₂BR

JOMC 156 101 (1978)

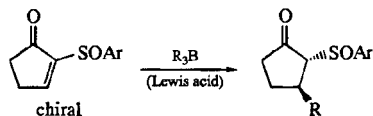
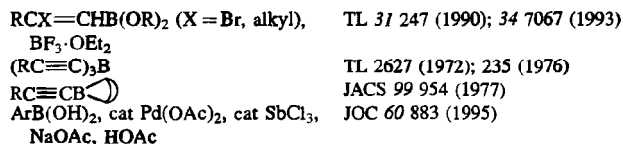


JACS 98 7832 (1976)

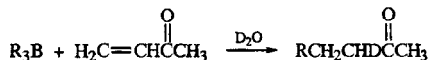
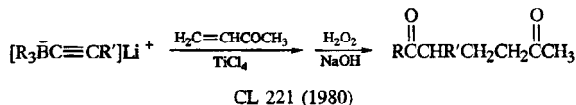


JACS 107 5225 (1985)

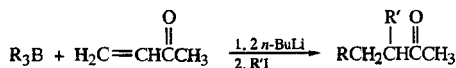
(X = Br, I)



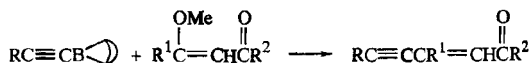
JACS 115 10464 (1993)



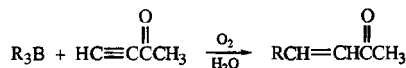
JACS 89 5708 (1967); 91 6195 (1969)



JOC 36 1790 (1971)



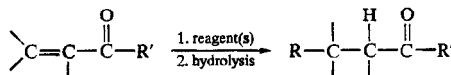
JOC 42 3106 (1977)



JACS 92 3503 (1970)

4. Organoaluminum, -gallium and -thallium Compounds

See also page 1596, Section 16 and page 1599, Section 18.

R

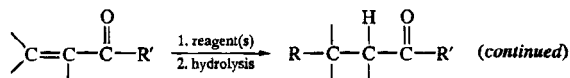
Me

Me or Ph

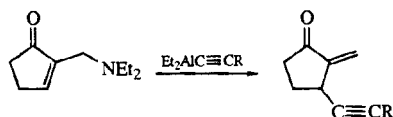
Reagent(s)LiTlMe₄R₂Al (R = Me, Ph)

TL 33 1763 (1992)

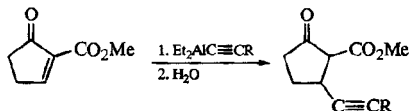
JOC 44 4792 (1979)



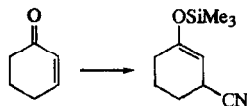
<u>R</u>	<u>Reagent(s)</u>	
<i>n</i> -Bu	LiTlMe ₂ (<i>n</i> -Bu) ₂	TL 33 1763 (1992)
Me, CH=CH ₂ , CH ₂ CH=CH ₂ , RC≡C, 2-furyl	LiAlRMe ₃ , R ₃ SiOTf	SL 163 (1995)
<i>E</i> -CH=CHR	[<i>E</i> -RCH=CHAlMe(<i>i</i> -Bu) ₂] ₂ Li	TL 4083 (1972); 765 (1975) JOC 44 71, 1438 (1979)
C≡CR	Et ₂ AlC≡CR (RC≡C) ₃ Al (Ga) LiTlMe ₃ (C≡CR)	JACS 93 7320 (1971) TL 2627 (1972) TL 33 1763 (1992)
CN	Et ₂ AlCN or Et ₃ Al-HCN	JACS 94 4635, 4644, 4654, 4672 (1972); 110 1985 (1988) Org Syn 52 100 (1972) TL 5113 (1973); 28 1439 (1987) Org Rxn 25 255 (1977) Syn Commun 8 231 (1978) JOC 51 902 (1986); 57 3347 (1992); 60 5560 (1995) Org Syn Coll Vol 6 14 (1988) JOC 59 311 (1994) JOC 59 2766 (1994)
	Et ₂ AlCN, KCN, 18-crown-6 HCN, Et ₂ AlCl	

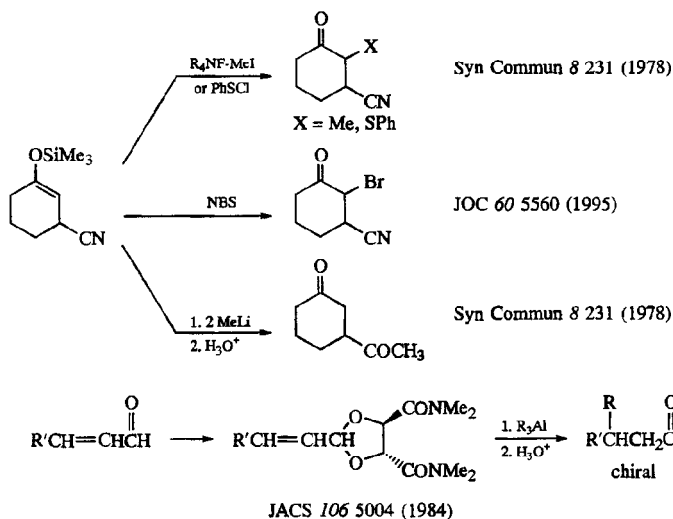


JOC 56 3205 (1991)

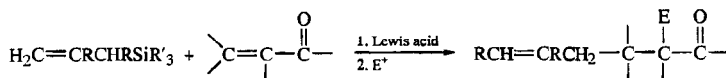


TL 27 2885 (1986)

Et₂AlCN/Me₃SiCl, pySyn Commun 8 231 (1978)
JACS 111 5761 (1989)Et₃Al, Me₃SiCNTL 21 3389 (1980)
Tetr 39 967 (1983)



5. Organosilicon Compounds


$$\underline{\text{E}^+}$$
$$\text{H}_2\text{O}$$

JACS 99 1673 (1977); 104 1124 (1982) (intramolecular); 106 721 (1984); 107 2568 (1985); 108 3835 (1986); 110 6556 (1988); 111 3336 (1989); 114 7375 (1992)

TL 1385 (1977); 4557 (1979); 21 955, 4557 (1980); 22 485 (1981); 28 1483, 5441, 5793, 6413 (1987); 30 197, 2465 (1989); 33 1469 (1992); 34 2613 (1993) (intramolecular); 35 8247 (1994) (intramolecular)

CC 525 (1979)

Syn 446 (1979)

CL 609, 961 (1982)

Pure Appl Chem 54 1 (1982) (review)

JOC 49 4214 (1984); 54 1548 (1989); 55 4392 (1990); 56 387 (1991); 58 4471, 5931 (1993)

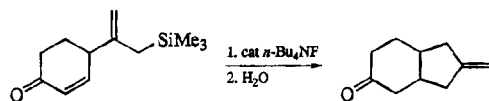
Org Syn 62 86 (1984)

Org Syn Coll Vol 7 443 (1990)

SL 279, 766 (1992); 463 (1994) (Amberlyst 15, intramolecular)

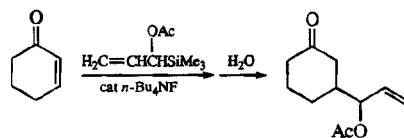
$$\text{RCHO}, \text{R}_2\text{CO}, \text{RCH(OR)}_2, \text{HC(OR)}_3, \text{RCOCl}$$

CL 245 (1979)

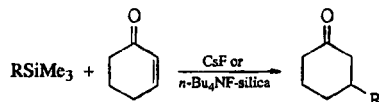


TL 26 2747, 2751 (1985); 29 2773 (1988)

JOC 51 1753 (1986)



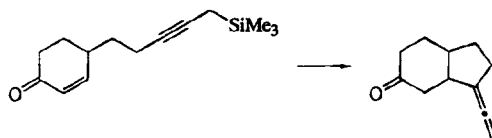
TL 28 4649 (1987)



R = allyl, benzyl, heterocyclic, ArCR(OR)

TL 23 5079 (1982)

JOC 56 5213 (1991)



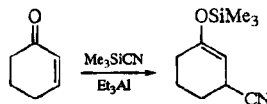
Amberlyst 15

SL 463 (1994)

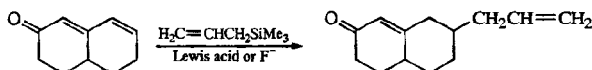
TL 36 4051 (1995)

EtAlCl₂ or TiCl₄

JOC 53 3823 (1988) (enone and dienone)



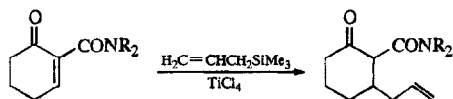
See page 1589, Section 4.



TL 26 2747, 2751 (1985) (both intramolecular); 29 1533, 2773 (intramolecular) (1988); 31 51, 2239 (1990) (both intramolecular)

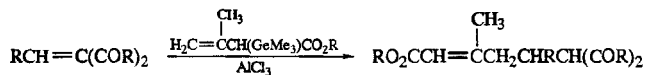
JOC 53 50, 3823 (1988) (both intramolecular); 56 3958, 3973, 3988 (1991) (all intramolecular); 58 1030 (1993) (intramolecular)

SL 463 (1994) (Amberlyst 15, intramolecular)



TL 33 4397 (1992)

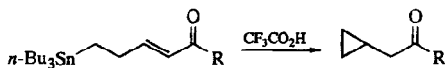
6. Organogermanium Compounds



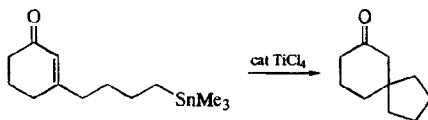
TL 32 4749 (1991)

7. Organotin Compounds

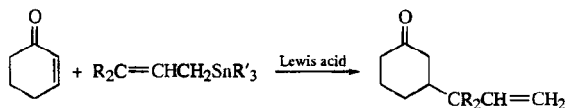
See also page 1596, Section 16; and page 1598, Section 17.



TL 23 2577 (1982)



JACS 102 2113 (1980)

Lewis acidBF₃·OEt₂

TL 28 1483 (1987)

JOC 53 3597 (1988)

AlCl₃

TL 28 1483 (1987)

JOC 53 3597 (1988)

(Et₂Al)₂SO₄

CL 977 (1979)

R₃SiOTf

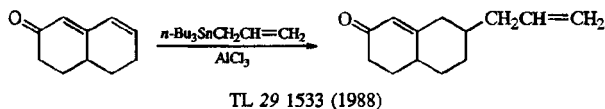
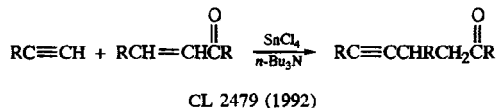
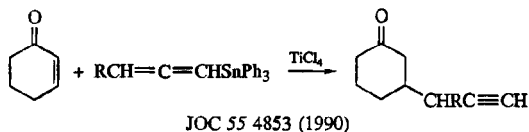
Syn Commun 21 25 (1991)

TL 35 4279 (1994)

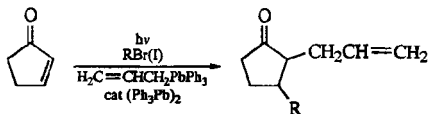
TiCl₄

TL 28 1483 (1987)

JOC 53 3597 (1988)



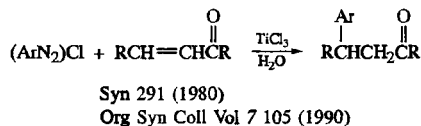
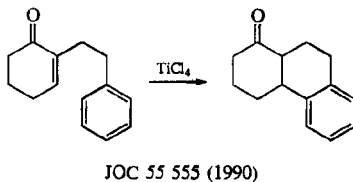
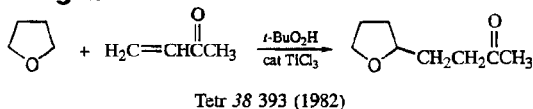
8. Organolead Compounds

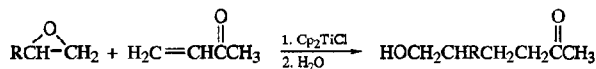


9. Organostibine Compounds

See page 1598, Section 17.

10. Titanium Reagents





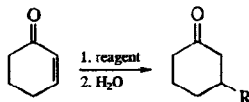
JACS 111 4525 (1989)

11. Organozirconium Compounds

See page 1596, Section 16; and page 1599, Section 18.

12. Organomanganese Compounds

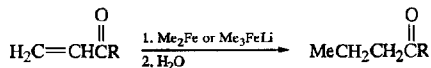
See also page 1599, Section 18.



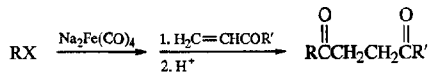
Reagent

R₂Mn (R = 1° alkyl, aryl) TL 27 569 (1986)RMnCl, R₂Mn or R₃MnLi (R = Me, *n*-Bu) TL 25 293 (1984)

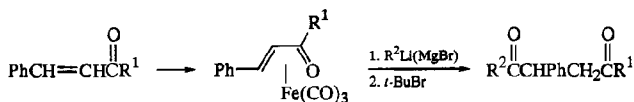
13. Organoiron Compounds



TL 31 1553 (1990)

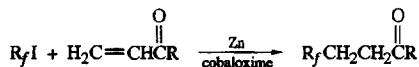


JACS 99 5222 (1977)

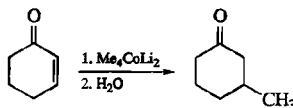


CC 226 (1987)

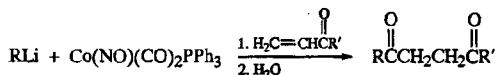
14. Organocobalt Compounds



JOC 57 3339 (1992)

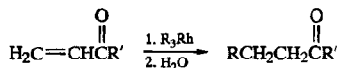


TL 31 511 (1990)

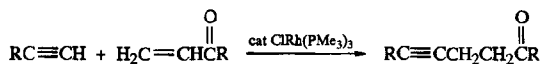


JOC 50 4955 (1985)

15. Organorhodium Compounds

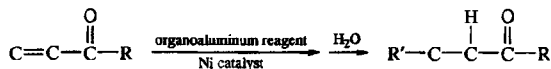


TL 31 1553 (1990)

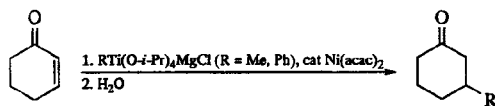


TL 31 7063 (1990)

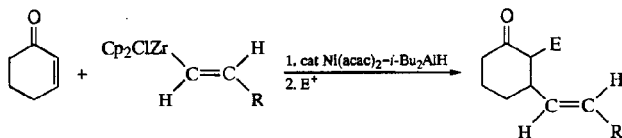
16. Organonickel Compounds



<u>R</u>	<u>R'-Al</u>	<u>Ni catalyst</u>	
H	Me ₃ Al	Ni(acac) ₂	SL 679 (1994)
alkyl, aryl	Me ₃ Al	Ni(acac) ₂	JOC 39 3297 (1974) Austral J Chem 28 801, 817 (1975)
	LiAlMe ₄	Ni(acac) ₂	JOC 39 3297 (1974)
	Me ₂ AlC≡CR	Ni(acac) ₂ -i-Bu ₂ AlH	JACS 100 2244 (1978)
			JOC 45 3053 (1980)



TL 35 6075 (1994)

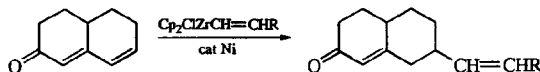
 E^+
H

JACS 99 8045 (1977); 102 1333 (1980); 103 4466 (1981)

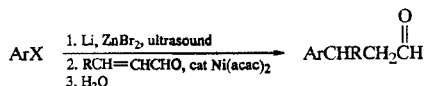
TL 4383 (1978); 31 7555 (1990)

 H_2CO

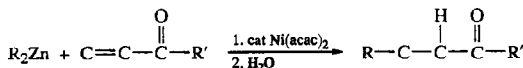
TL 4381 (1978)



JACS 103 4466 (1981)



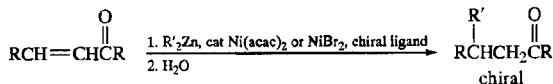
TL 26 829 (1985)



JOC 48 3837 (1983); 49 931 (1984); 50 5761 (1985)

JACS 109 4752 (1987); 111 5761 (1989)

TL 29 2787 (1988)



JOC 53 4148 (1988); 60 3626 (1995)

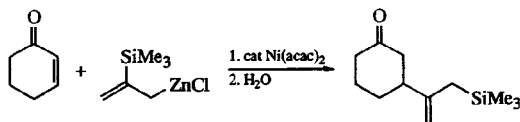
CL 1571 (1988)

CC 516 (1989)

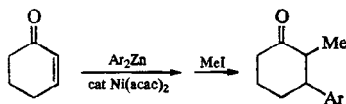
TL 31 5011 (1990)

SL 439 (1992)

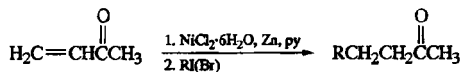
Ber 125 1205, 1781 (1992)



SL 279 (1993)

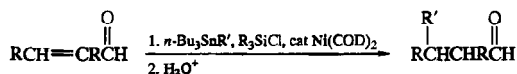


JOC 50 5761 (1985)

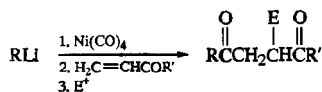
 $\text{R} = 1^\circ$ alkyl, vinylic

TL 30 689 (1989)

JOC 60 6574 (1995)

 $\text{R}' = \text{vinylic, Ac}$

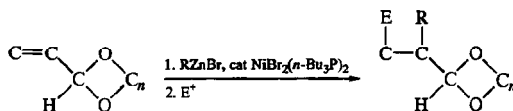
JACS 114 5160 (1992)

 E^+ H_2O

JACS 91 4926 (1969)

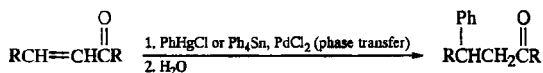
 $\text{H}_2\text{C}=\text{CHCH}_2\text{I}$

JOC 47 4382 (1982)

 $n = 2, 3$; $\text{R} = \text{benzylic, allylic}$; $\text{E}^+ = \text{H}_2\text{O}$, RX ($\text{CuCN} \cdot 2\text{LiCl}$), I_2

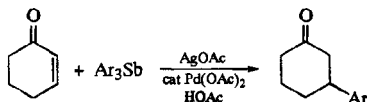
JACS 111 366 (1989)

17. Organopalladium Compounds

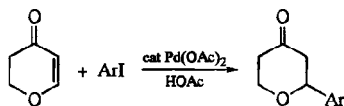


TL 4591 (1979)

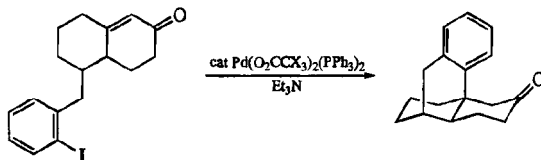
Tetr 37 2941 (1981)



TL 35 1275 (1994)



JOC 57 4612 (1992)



TL 35 3453 (1994) (X = F); 36 7047 (1995) (X = H)

18. Organocopper Compounds

Reviews and key references:

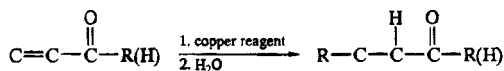
Org Rxs 19 1 (1972); 41 135 (1992)

G. H. Posner, "An Introduction to Synthesis Using Organocopper Reagents," J. Wiley, New York (1980)

Tetr 40 5005 (1984) (higher order cuprates)

TL 32 447 (1991) (various reagents)

R. A. J. Smith and A. S. Vellekoop, "Advances in Detailed Reaction Mechanisms," Ed. J. M. Coxon, JAI Press, Greenwich, CT (1994), Vol 3, p 79



Copper reagent

RBr, Li, CuI or $n\text{-C}_3\text{H}_7\text{C}\equiv\text{CCu}\cdot\text{P}(\text{NMe}_2)_3$, ultrasound (R = 1°, 3° alkyl; aryl; allyl; vinyl) JOC 47 3805 (1982)

RX, Zn, CuI, ultrasound (R = 1°, 2°, 3° alkyl; X = Br, I) TL 27 3149 (1986); 29 1203, 5369, 5373 (1988); 33 5189, 8069 (1992); 35 275 (1994)
JOC 58 118 (1993)

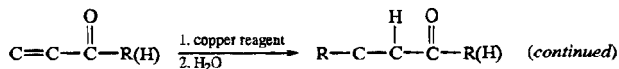
$n\text{-Bu}_3\text{SnCHRI}$, Zn-Cu/CuCN SL 891 (1992)
RX (R = 1°, 2° alkyl; X = Br, I), SmI_2 /CuI-P(OEt)₃ JOC 57 1740 (1992)


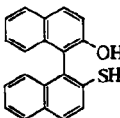



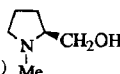
RX (R = 1°, 2° alkyl; X = Br, I), SmI_2 /cat CuBr-SMe₂, Me₃SiCl, HMPA JOC 58 3455 (1993)

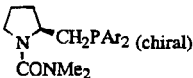
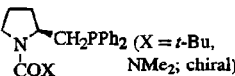
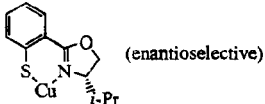
Li, naphthalene/CuI- $n\text{-Bu}_3\text{P}$, $n\text{-Bu}_3\text{P}$ /RBr (R = 1° alkyl) JOC 52 5056 (1987)

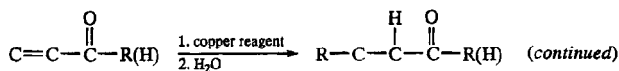
Li, naphthalene/CuCN- $n\text{LiX}$ (n = 1, 2; X = Cl, Br)/RX (1° or 2° alkyl Br, ArBr, allylic Cl) JACS 113 4672 (1991); 114 5110 (1992)
JOC 58 2483 (1993)

Li, naphthalene/CuI-LiCl/allylic chloride/Me₃SiCl TL 34 3063 (1993)



Copper reagent

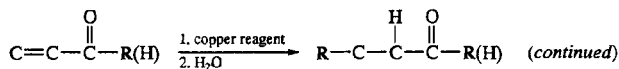
- Li, naphthalene / $\text{ThCu}(\text{CN})\text{Li}$ / RX ($\text{RX} = 1^\circ \text{RCl}; 1^\circ, 2^\circ \text{RBr}$) / Me_3SiCl JOC 58 2492 (1993)
- $\text{PhCHOHCH}(\text{CH}_3)\text{N}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$ / $\text{RLi}/\text{CH}_3\text{I}/\text{CuI}/\text{RLi}/\text{CH}_3\text{I}$ (chiral) JACS 108 7114 (1986)
- RLi , CuI, chiral $\text{MeNHCHArCH}_2\text{N}$  (enantioselective) JOC 60 8424 (1995)
- RLi , cat $\text{CuBF}_4(\text{MeCN})_4$, cat  SL 155 (1995)
- RLi , CuCN , LiBr ,  CH_2PPh_2 ($\text{X} = t\text{-Bu}$, NMe_2 ; chiral) TL 36 4273 (1995)
- MeLi , $(\text{CuSAr})_3$ JACS 114 3400 (1992)
- $\text{RCH}(\text{OR})\text{Li}$, CuX ($\text{X} = \text{I}, \text{CN}$), Me_3SiCl TL 27 4553 (1986)
- , cat $\text{CuBr}\cdot\text{SMe}_2$ JOC 56 3825 (1991)
- $\text{RC}(\text{CH}_2)_3\text{Li}$
- -Li, $\text{CuI}\cdot n\text{-Bu}_3\text{P}$, $\text{BF}_3\cdot\text{OEt}_2$ JACS 111 1381 (1989)
- RMgX , CuX JACS 86 269 (1964); 104 6879 (1982)
JOC 33 305 (1968); 42 1709 (1977)
BSCF 568 (1969)
TL 3361 (1979); 28 357, 3061 (1987)
CL 45 (1980) (chiral ligand)
JOMC 220 295 (1981)
Helv 64 1575, 2489 (1981)
- CH_3MgBr , CuBr /  (enantioselective) CL 45 (1980)
- RMgX , $\text{CuBr}\cdot\text{SMe}_2$ JACS 106 1443 (1984)
- RMgX , $\text{CuBr}\cdot\text{SMe}_2$, Me_3SiCl JACS 115 49 (1993)
- $\text{R}_2\text{C}=\text{CRCH}_2\text{MgX}$, $\text{CuBr}\cdot\text{SMe}_2$, Me_3SiCl , LiCl JOC 59 7437 (1994)
- RMgX , CuI , $\text{BF}_3\cdot\text{OEt}_2$ JOC 51 5311 (1986)
JACS 110 7445 (1988)
- RMgX , CuI , $n\text{-Bu}_3\text{P}$ JOC 59 6008 (1994)
- RMgX , cat CuBr Org Syn 65 203 (1987)
Org Syn Coll Vol 8 522 (1993)


$H_2C=CHC(=CH_2)MgCl$, cat $CuBr$, Me_2S	TL 24 1003 (1983)
$RMgX$, cat $CuBr \cdot SMe_2$	JOC 47 5045 (1982) JACS 114 7375 (1992)
$ArMgX$, cat $CuBr \cdot SMe_2$	TL 31 5401 (1990)
$RMgX$, cat $CuBr \cdot SMe_2$, Me_3SiCl , (HMPA)	TL 27 4025 (1986); 28 5669 (1987); 29 325 (1988); 30 2371, 7075 (1989); 33 3145 (1992) JOC 51 4323 (1986) Tetr 44 4757 (1988) SL 697 (1990)
$R_2C=CRCH_2MgX$, cat $CuBr \cdot SMe_2$, Me_3SiCl , $LiCl$	JOC 59 7437 (1994)
$RMgX$, cat CuI	JOC 53 2732 (1988)
$RMgX$, cat CuI , Me_3SiCl , (HMPA)	JOC 57 2469 (1992) TL 34 7291 (1993)
$RMgX$, cat CuI , cat  (chiral)	TL 36 4275 (1995)
$RMgX$, $CuCN$,  ($X = i\text{-Bu}$, NMe_2 ; chiral)	TL 36 4273 (1995)
$RMgX$, cat  (enantioselective)	TL 34 7725 (1993)
$RMgX$, cat $[CuSC_6H_4(CHMeNMe_2)_2]_3$ (enantioselective)	JACS 114 3400 (1992) TL 35 6135 (1994) Pure Appl Chem 66 1455 (1994)
$RMgX$, cat $Li[Cu_2R(\text{tropocoronand-5,5})]$	JACS 110 3175 (1988)
$RMgX$, cat $Li[CuR(\text{CHIRAMT})]$	JACS 110 3175 (1988)
$RCaX$, $ThCu(CN)Li$ ($R = 1^\circ$ alkyl, aryl)	JOC 55 5045 (1990)
Me_3Al , cat $CuBr$	SL 679 (1994) (enals)
Me_3Al , cat $CuBr$, Me_3SiCl	SL 679 (1994) (enals) TL 35 8591 (1994)
Me_3Al , cat $CuBr \cdot SMe_2$	JOC 60 6571 (1995)
Me_2AlOEt , cat $CuBr$	TL 35 8591 (1994)
$MeCR=CHAlMe_2 / (n\text{-BuC}\equiv\text{C})_2Cu(CN)Li_2$	JOC 55 1425 (1990); 57 3178, 5071 (1992)
$MeCR=CHAlMe_2$, cat $CuCN \cdot 2LiCl$	JOC 56 5761 (1991)
$RCH=CRSnMe_3$, $CuCl$	JOC 60 2322 (1995) (intramolecular)
$n\text{-Bu}_3SnCH=CHR$, $R_2Cu(CN)Li_2$	JACS 110 2641 (1988) TL 31 1857 (1990); 34 4579 (1993) JOC 58 3681 (1993)

Copper reagent

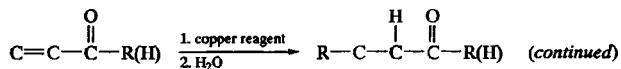
RCH=CHTeR' / R₂Cu(CN)Li₂	TL 33 5721 (1992)
RCH=CHCH=CHTeR' / R₂Cu(CN)Li₂	TL 33 5721 (1992)
RC≡CCH=CHTeR' / R₂Cu(CN)Li₂	TL 33 5721 (1992)
(RCH=CH)₂Te, ThCu(<i>n</i>-Bu)Cu(CN)Li₂	SL 671 (1995)
RTi(O-<i>i</i>-Pr)₄Li, Me₃SiX (X = Cl or OTf), cat CuI·2LiCl	JOC 56 5489 (1991)
RZrClCp₂, cat CuBr·SMe₂	JOC 56 6494 (1991); 60 4316 (1995) TL 35 4669 (1994); 36 1805 (1995) Tetr 50 1935 (1994)
RCH₂CH[B(OR)₂]ZrClCp₂, cat CuBr·SMe₂	TL 36 1805 (1995)
Cp₂Zr(Cl)CH=CHR, cat CuOTf, LiI	TL 1303 (1977)
Cp₂MeZrCH=CHR / Me₂Cu(CN)Li₂	JACS 112 7440 (1990) TL 35 4669 (1994)
Cp₂Zr(Cl)CH=CHR / 2 RLi / CuCN / MeLi	JACS 112 7441 (1990)
Cp₂Zr(Cl)CH=CHR / 3 MeLi / CuCN·2LiCl	JACS 112 7440 (1990)
Cp₂Zr(Cl)CH=CHR / CuCN / 3 MeLi	JOC 56 2549 (1991)
Cp₂Zr(Cl)CH=CHR, Me₂Cu(CN)Li₂	JACS 114 7919 (1992)
Cp₂Zr(Cl)CH=CHR / MeLi / cat Me₂Cu(CN)Li₂ / Me₃ZnLi	JACS 115 12625 (1993); 116 11689 (1994) TL 35 6433 (1994)
Cp₂Zr(Cl)CH=CHR / 2 MeLi / ThCu(CN)Li	JACS 112 7440 (1990)
RMnCl, cat CuCl (R = 1°, 2°, 3° alkyl; aryl; vinylic)	TL 30 3541, 7365 (1989)
RZnX / MeLi / cat Me₂Cu(CN)Li₂ / Me₃SiCl	JACS 117 6126 (1995)
RZnX, ThCu(CN)Li, BF₃·OEt₂ or Me₃SiCl	JOC 56 1445 (1991)
R₂Zn, CuCN·2LiCl, Me₃SiCl	JOC 57 1965 (1992)
Zn(CH₂CH₂CO₂R)₂, cat CuBr·SMe₂, Me₃SiCl	JACS 106 3368 (1984); 109 8056 (1987) JOC 54 3334 (1989) Org Syn Coll Vol 8 277 (1993)
Zn(CH₂CH₂CO₂R)₂, cat CuBr·SMe₂, BF₃·OEt₂, HMPA	JOC 51 4323 (1986) JACS 111 6257 (1989)
RCu	JOC 33 949 (1968) TL 28 2525 (1987)
RCu·<i>n</i>-Bu₂S (R = 2-pyridyl)	Tetr 38 1509 (1982)
RCu·<i>n</i>-Bu₃P	JOC 31 3128 (1966); 33 949 (1968) Tetr 38 1509 (1982)

$RCH=CHCu \cdot n-Bu_3P$	JOC 52 3346 (1987) TL 31 3313 (1990)
$RCu \cdot 2n-Bu_3P$	TL 21 1247 (1980)
$RCH=CHCu \cdot 2n-Bu_3P, Me_3SiCl$	JACS 114 8008 (1992)
$RCu, n-Bu_3P, BF_3 \cdot OEt_2$	TL 28 1973 (1987); 32 4565 (1991)
$RCu[P(OR')_3]_3$ ($R' = Me, n-Bu$)	JOC 33 949 (1968)
RCu , chiral P ligand (enantioselective)	JACS 113 6332 (1991)
$RCu \cdot BF_3$	JACS 100 3240 (1978); 104 6081 (1982); 111 1826 (1989) JOC 47 119 (1982) TL 28 2525 (1987); 32 4565 (1991)
$ROCH_2Cu, i-Pr_2S, BF_3 \cdot OEt_2$	JACS 109 4930 (1987)
$RCu \cdot AlCl_3$	CC 1193 (1980); 703 (1982) (β -cyclopropyl- α , β -enones) TL 21 4073 (1980)
$RCu, Me_3SiCl, (HMPA)$	TL 27 4029 (1986); 28 2525 (1987)
$PhCH_2Cu, Me_3SiCl, HMPA$ or TMEDA	TL 33 2383 (1992)
$R_2C=CRCH_2Cu, Me_3SiCl$	JACS 112 4404 (1990)
RCu, Me_3SiI	JOC 58 7238 (1993)
R_2CuLi	JOC 31 3128 (1966); 33 949 (1968); 35 186 (1970); 41 3629, 4031 (1976); 44 4481 (1979); 48 1404 (1983); 51 4779 (1986); 54 3882 (1989); 60 903 (1995) (chiral Re-complexed enone, enantioselective) TL 2875, 3795 (1971); 3361, 3365 (1979); 22 3585 (1981); 23 3823 (1982) (chiral R); 28 2525, 4251, 4943 (1987); 29 439 (1988); 31 623, 1393 (1990); 32 4565 (1991); 33 7521 (1992) Tetr 35 2645 (1979) (α -haloenones); 36 2305 (1980) (enals); 37 1385 (enals), 3981, 4027 (1981); 38 1509 (1982) CC 643 (1981) (enals) JACS 107 2149 (1985); 109 5731 (1987); 111 8276 (1989) (mechanism); 116 2902 (mechanism), 3312 (1994); 117 5245 (1995)
R_2CuLi ,  CH_2PPh_2 (enantioselective) CO- <i>t</i> -Bu	TL 33 7193 (1992)
R_2CuLi , various chiral P ligands (enantioselective)	JACS 113 6332 (1991)
polymer- $PPh_2 \cdot R_2CuLi$	JOC 44 2705 (1979)
Me_2CuLi ,  CH_2OCH_3 (enantioselective) <i>t</i> -BuS R	TL 24 3517 (1983)

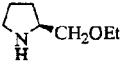
Copper reagent

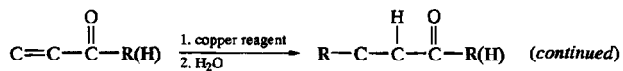
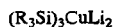
$[\text{Me}_3\text{Si}(\text{PhS})\text{CH}]_2\text{CuLi}$	JOC 51 3983 (1986)
$(t\text{-BuOCH}_2)_2\text{CuLi}$	JOC 55 4712 (1990)
$(\text{ROCH}_2)_2\text{CuLi}$, $i\text{-Pr}_2\text{S}$	JACS 109 4930 (1987)
$(\text{ROCH}_2)_2\text{CuLi}$, $\text{BF}_3\cdot\text{OEt}_2$, $i\text{-Pr}_2\text{S}$	JACS 109 4930 (1987)
$(\text{ROCH}_2)_2\text{CuLi}$, Me_3SiCl , $i\text{-Pr}_2\text{S}$	JACS 109 4930 (1987)
$(\text{LiOCH}_2\text{CMe}_2\text{CH}_2)_2\text{CuLi}$	JOC 54 5657 (1989)
R_2CuLi , $\text{BF}_3\cdot\text{OEt}_2$	Tetr 37 3981 (1981) JACS 103 194 (1981); 108 3443 (1986); 111 1351 (1989) TL 28 4061 (1987)
R_2CuLi , Me_3SiCl , (HMPA)	TL 26 6015, 6019 (1985); 27 1047, 4029 (1986); 29 439, 4189 (1988); 30 3685, 7087 (1989); 32 4565 (1991); 33 7521 (1992); 34 6689 (1993) JOC 58 2530 (1993) JACS 117 11023 (1995)
R_2CuLi , Me_3SiCN	TL 34 6689 (1993)
$(\text{C}_6\text{H}_5)_2\text{CuLi}$	TL 1579, 1583 (1970); 28 3065 (1987)
$(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{CuLi}$	JOC 34 3615 (1969)
$(\text{RCH}=\text{CH})_2\text{CuLi}$	Can J Chem 48 1626 (1970) Helv 54 1939 (1971) JACS 93 7318 (1971); 94 9256 (1972) TL 2455 (1971); 2627 (1972) JOC 42 1709 (1977)
$(\text{H}_2\text{C}=\text{CH})_2\text{CuLi}$, Me_3SiCl	JACS 109 7575 (1987); 111 2984 (1989)
$(\text{PhMe}_2\text{Si})_2\text{CuLi}$	TL 28 965 (1987) (enal)
$[\text{Ph}_2(\text{Et}_2\text{N})\text{Si}]_2\text{CuLi}$	JOC 59 4370 (1994)
R_2CuMgX	JOMC 199 9 (1980); 228 321 (1982) (enals)
$(\text{PhCH}_2)_2\text{CuMgCl}$	TL 33 2383 (1992)
$(\text{RCH}=\text{CH})_2\text{CuMgX}$	JOC 53 3617 (1988); 55 3164 (1990) TL 31 6027 (1990)
Me_2CuMgX ,  CH_2OH (enantioselective)	TL 22 3601 (1981)
$\text{R}_2\text{CuMgX}\cdot\text{COD}$	TL 21 1311 (1980)
R_2CuMgX , Me_3SiCl	TL 30 3685 (1989)
$(\text{R}_2\text{C}=\text{CR})_2\text{CuMgX}$, Me_3SiCl	TL 31 6027 (1990)

MeCuRLi	TL 21 3151 (1980)
PhCuRLi (R = 2-pyridyl)	Tetr 38 1509 (1982)
ArCuRLi	Tetr 34 3023 (1978) Acta Chem Scand B 32 483 (1978)
2,4,6-Me ₃ C ₆ H ₂ CuRLi	TL 22 192 (1981) JOC 46 192 (1981) (enals and enones)
ThCuArLi	TL 23 3823 (1982)
ThCuRLi, Me ₃ SiCl	TL 34 6689 (1993)
ThCuRLi, Me ₃ SiCN	TL 34 6689 (1993)
ThCuR(CN)Li ₂	TL 25 5959 (1984) (R = vinylic); 28 945 (1987); 30 4379 (1989) (R = vinylic); 31 623 (1990); 35 5417 (1994) JOMC 285 437 (1985) JACS 110 8129 (1988); 115 6101 (1993) (R = vinylic) JOC 59 6153 (1994) (R = vinylic)
ThCuR(CN)Li ₂ , BF ₃ ·OEt ₂	TL 25 5959 (1984) (R = vinylic) JOC 55 5711 (1990) (R = aryl)
ThCuR(CN)Li ₂ , Me ₃ SiCl (R = vinylic)	JACS 113 5085 (1991); 115 3966 (1993) JOC 57 5250 (1992)
ThCuCH=CHSn(<i>n</i> -Bu) ₃ (CN)Li ₂	TL 33 49 (1992)
ThCu(SnMe ₃)(CN)Li ₂	JOC 53 5366 (1988)
(<i>n</i> -PrC≡CCuR)Li (or MgX)	JACS 94 7210 (1972); 106 8296 (1984); 111 2737 (1989) JOC 44 3661 (1979) TL 29 4909 (1988) (R = vinylic)
(<i>t</i> -BuC≡CCuR)Li	JOC 38 3893 (1973); 44 1006 (1979)
(<i>n</i> -C ₅ H ₁₁ C≡CCuCH=CHR)Li · P(NMe ₂) ₃ , (MgBr ₂)	JOC 55 3164 (1990)
[<i>n</i> -C ₅ H ₁₁ C≡CCuCH=CHSn(<i>n</i> -Bu) ₃ Li]	TL 28 3065 (1987)
(MeOCMe ₂ C≡CCuR)Li	JOC 43 3418 (1978)
(Me ₂ NCH ₂ C≡CCuR)Li	JOC 44 1006 (1979)
(Me ₃ SiC≡CCuCH ₂ CH=CROSiMe ₃)M (M = Li, MgBr)	TL 25 5307 (1984) JACS 107 5495 (1985)
(Me ₃ SiC≡CCuCH ₂ CH=CROSiMe ₃)Li, Me ₃ SiCl, HMPA	TL 27 4029 (1986)
[Me ₃ SiC≡CCuCH=C=CROSiMe ₂ (<i>t</i> -Bu)]Li	TL 28 1299 (1987)
RCu(CN)Li (or MgX)	CC 88 (1973) TL 3879 (1977); 22 2985 (1981) JACS 114 3983 (1992) (R = aryl)

**Copper reagent**

$\text{PhCH}_2\text{Cu}(\text{CN})\text{MgCl}$	TL 33 2383 (1992)
$\text{RCu}(\text{CN})\text{Li}$, LiBr, chiral ligand (enantioselective)	TL 35 895 (1994)
$\text{R}_3\text{SiCu}(\text{CN})\text{Li}$	JOC 56 770 (1991)
$\text{RCu}(\text{CN})\text{Li}$, R_3SiCl	TL 26 6019 (1985) (enals); 30 3685 (1989); 31 3995 (1990) JOC 55 5477 (1990)
$\text{RN}(\text{Boc})\text{CHRCu}(\text{CN})\text{Li}$, Me_3SiCl	SL 407 (1993)
$\text{RCu}(\text{CN})\text{ZnX}$	TL 30 5069 (1989); 31 7575 (1990); 34 5261 (1993) JOC 56 3205 (1991)
$\text{ArCH}_2\text{Cu}(\text{CN})\text{ZnX}$	JOC 53 5789 (1988)
$\text{RCu}(\text{CN})\text{ZnX}$, $\text{BF}_3 \cdot \text{OEt}_2$	TL 29 6693 (1988) JOC 54 5202 (1989); 58 588 (1993)
$\text{RCu}(\text{CN})\text{ZnX}$, $\text{BF}_3 \cdot \text{OEt}_2$, Me_3SiCl	JOC 56 1445 (1991)
$\text{RCu}(\text{CN})\text{ZnX}$, Me_3SiCl	JOC 53 2390 (1988); 54 5202 (1989); 56 1445, 5974 (1991); 58 588 (1993) TL 29 2395, 3887 (1988); 31 1833, 4481 (1990); 34 5597 (1993)
$\text{ArCu}(\text{CN})\text{ZnX}$	TL 31 4413 (1990)
$\text{ArCu}(\text{CN})\text{ZnX}$, $\text{BF}_3 \cdot \text{OEt}_2$, Me_3SiCl	JOC 56 1445 (1991)
$\text{RCH}=\text{CHCu}(\text{CN})\text{ZnI}$, Me_3SiCl	TL 33 3717 (1992)
$\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$	TL 23 3755 (1982); 28 2525 (1987); 29 439 (1988); 31 623, 4539 (R = allylic) (1990); 32 4081, 4451, 4565 (1991); 33 5693 (1992) JOC 49 3938 (1984); 51 1293 (1986); 57 2469 (1992) JACS 115 6101 (1993) (R = aryl, vinylic); 117 5245 (1995)
$(\text{RCH}=\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2$	JOC 53 3617 (1988); 57 2469 (1992) TL 32 4451 (1991)
$(\text{R}_3\text{SnCH}=\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2$, (LiCl)	TL 33 49 (1992); 36 8749 (1995)
$(\text{R}_3\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$	JOC 56 770 (1991)
$\text{RCH}=\text{CHCu}(\text{Me})(\text{CN})\text{Li}_2$	JOC 56 2549 (1991) JACS 115 6101 (1993)
$\text{Me}_3\text{SnCH}=\text{CHCH}=\text{CHCuR}(\text{CN})\text{Li}_2$ (R = Me, 2-thienyl, $\text{MeOCMe}_2\text{C}=\text{C}$)	TL 32 7211 (1991)

$R_3Si(Me)Cu(CN)Li_2$	JOC 56 770 (1991)
$R_3Sn(Me)Cu(CN)Li_2$	JOC 56 770 (1991)
$Me_3Sn(n-Bu)Cu(CN)Li_2$	TL 30 4617 (1989)
$R_2Cu(CN)(MgX)_2$	JACS 117 5245 (1995)
$(H_2C=CH)_2CuCN(MgX)_2$	JOC 53 3617 (1988)
$R_2Cu(CN)Li_2, BF_3 \cdot OEt_2$	TL 25 5959 (1984) (R = Ph); 29 2031 (R = CH=CH ₂), 3045 (R = 2-furyl), 4189 (1988) JOC 52 4647 (1987)
$R_2Cu(CN)Li_2, Me_3SiCl$	TL 29 439, 4189 (1988); 34 3247 (1992)
$(R'OCHR)_2Cu(CN)Li_2, Me_3SiCl$	TL 28 3911 (1987); 29 3911 (1988) JACS 110 6249 (1988) JOC 55 5428 (1990)
$[RN(Boc)CHR]_2Cu(CN)Li_2, Me_3SiCl$	SL 407 (1993)
$RCu(NC_2)_2Li$	JACS 104 5824 (1982)
$RCu(NR'_2)_2Li$ (chiral amides, enantioselective)	JOC 51 4953 (1986) JACS 109 2041 (1987) TL 31 965, 4105 (1990); 32 3973 (1991)
$MeCu(X)Li$ (X = chiral amide or alkoxide, enantioselective)	Bull Soc Chim Belg 87 369 (1978)
$\begin{array}{c} X \\ \diagup \quad \diagdown \\ N \\ \diagdown \quad \diagup \\ CuR(CN)Li_2 \end{array}$ (X = CH, N)	TL 33 1041 (1992)
$RCu(PPh_2)_2Li$	JACS 104 5824 (1982)
$RCuP(t-Bu)_2Li$	JACS 110 7226 (1988)
$RCu(OR')Li$ (R' = <i>t</i> -Bu, chiral R'; enantioselective)	JACS 95 7788 (1973) TL 1815 (1973); 22 1329 (1981); 24 3165 (1983) Acta Chem Scand B 34 443 (1978)
$Me_2Cu(OR')Li_2$ (chiral R', enantioselective)	SL 351 (1994)
$CuSCN / 2 H_2C=C(Me)Li / 2$  CH_2OEt (enantioselective)	TL 33 3469 (1992)
$RCu(SR')Li$ (R' = Ph, chiral R'; enantioselective)	JACS 95 7788 (1973) Syn 662 (1974) Acta Chem Scand B 34 443 (1978) TL 3849 (1980)
$RCu(CH_2SOCH_3)_2Li$	JOC 52 1885 (1987)
$RCu(CN)(CH_2SOCH_3)_2Li_2$	JOC 52 1885 (1987)
$RCu(CH_2SO_2R')Li$ (R' = Me, Ph)	CC 358 (1982)
Me_3CuLi_2	TL 2659 (1976)
Me_3CuLi_2, Me_3Cu_2Li , or $Me_5Cu_3Li_2$	JOC 42 1099 (1977)

Copper reagent

JOC 56 770 (1991)



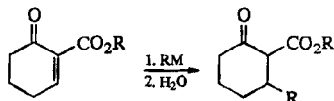
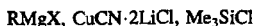
JACS 111 1351 (1989)



CC 643 (1981) (enals)

JOC 47 2572 (1982) (enals)

See also page 452, Section 2.28.

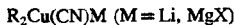
RM

JOC 60 2664 (1995)



JACS 109 6199 (1987)

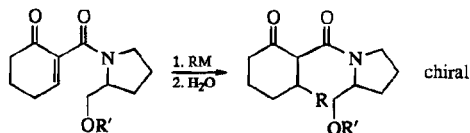
TL 34 7789 (1993); 36 7233 (1995)



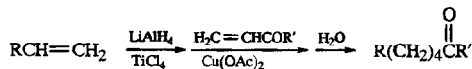
TL 32 3643 (1991)



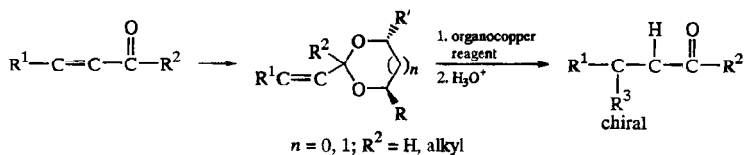
TL 32 3643 (1991); 36 4773, 7229 (1995)



JACS 113 4926 (1991)



CL 167 (1979)



Organocopper reagentPhCu, BF₃·OEt₂

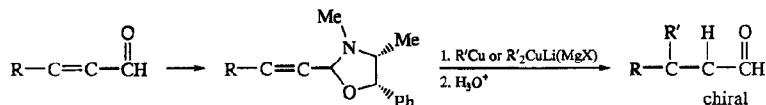
TL 27 3143 (1986)

R³Cu, CuBr, *n*-Bu₃P (R³ = aryl, vinylic)

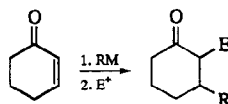
TL 28 2363 (1987)

Me₂CuLi, BF₃·OEt₂

TL 25 3083 (1984)



TL 24 373, 585 (1983)



Review: Syn 364 (1985)

E⁺RMR³XRLi, CuI, *n*-Bu₃P

JACS 110 1985 (1988)

RCH=CHLi, CuI, 2 *n*-Bu₃P

JACS 110 4726 (1988)

RMgX, cat CuBr·SMe₂

JOC 58 6807 (1993)

RMgX, CuBr·SMe₂

JOC 44 3731 (1979)

RMgX, cat CuI·*n*-Bu₃P

TL 29 5025 (1988)

JACS 103 4136 (1981); 108

3435 (1986); 109 6199

(1987)

JOC 58 6807 (1993)

R₂CuLi

JOC 38 4450 (1973); 29 275

(1974)

JACS 95 6867 (1973); 97 107

(1975); 101 938 (1979)

TL 2591 (1974); 4867 (1976);

27 5103, 6295 (1986); 29

1207 (1988) (R = vinylic); 31

4759 (1990)

CC 28 (1984)

(H₂C=CH)₂Cu(CN)Li₂

TL 27 5103 (1986)

(n-PrC≡CCuCH=CHR)Li

JCS Perkin I 1407 (1981)

TL 23 327 (1982)

RC≡CCH₂OTfCp₂Zr(Cl)CH=CHR / MeLi /

JACS 116 11689 (1994)

cat Me₂Cu(CN)Li₂ / Me₃ZnLi*n*-Bu₃SnCH=CHR, Me₂Cu(CN)Li₂ /

JOC 55 4209 (1990)

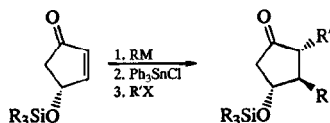
Me₃SiCl / MeLiH₂CO(H₂C=CH)₂CuMgBr

JOC 55 3954 (1990)

(RCH=CHCH=CH)₂Cu(CN)Li₂

SL 51 (1992)

<u>E</u> ⁺	<u>RM</u>	
R'CHO	RCu, PR ₃ RMgX, CuI H ₂ C=CHMgBr, cat CuI, TMEDA (RCH=CHCuC≡C- <i>n</i> -Pr)Li RCH=CHSn(<i>n</i> -Bu) ₃ / <i>n</i> -BuLi/ CuI/ <i>n</i> -Bu ₃ P Cp ₂ Zr(Cl)CH=CHR/MeLi/ cat Me ₂ Cu(CN)Li ₂ /Me ₃ ZnLi RZrClCp ₂ , cat CuBr·SMe ₂	TL 23 4057 (1982) TL 28 2489 (1987); 29 521 (1988) JOC 60 7837 (1995) TL 36 273 (1995) TL 29 6769 (1988) JACS 115 12625 (1993); 116 11689 (1994) TL 35 6433 (1994) Tetr 50 1935 (1994)
R'CHO (ZnCl ₂)	R ₂ CuLi, (PR ₃)	Helv 57 1317 (1974) JACS 96 7114 (1974); 97 6260 (1975) Tetr 35 425 (1979) JOC 46 2932 (1981)
R'COCl	R ₂ CuLi	Helv 57 1317 (1974) TL 1535 (1975); 21 2337 (1980) Tetr 33 1105 (1977) JOC 46 3719 (1981) JCS Perkin I 1994, 2394 (1981)
ClCO ₂ Me	RMgX, CuI R ₂ CuLi (<i>n</i> -PrC≡CCuCH=CHR)Li	JCS Perkin I 1516 (1981) TL 23 703 (1982) JOC 40 1488 (1975) TL 4087 (1976)
CO ₂ /CH ₂ N ₂	R ₂ CuLi	Tetr 35 425 (1979) CL 57 (1982) JACS 106 2954 (1984)
H ₂ C=C(SMe)SOMe	R ₂ CuLi	JOC 44 3755 (1979)
Br ₂	Ph ₂ CuLi R ₂ CuLi(MgX)	JACS 101 934 (1979) JOMC 228 321 (1982) (on enals)
PhSSPh	(<i>n</i> -PrC≡CCuCH=CHR)Li	TL 4091 (1976)
PhSCl	RCH=CHCu(SPh)Li	TL 4091 (1976)
MeSOCl	R ₂ CuLi	CL 1159 (1981)
PhSeBr	RMgX, CuI (CH ₃) ₂ C=CHMgBr, cat CuI R ₂ CuLi	Tetr 38 1959 (1982) JOC 50 2539 (1985) JOC 39 2133 (1974) JACS 97 5434 (1975)
<i>t</i> -BuO ₂ CN=NCO ₂ - <i>t</i> -Bu	RMgX, cat CuBr	TL 32 6851 (1991)

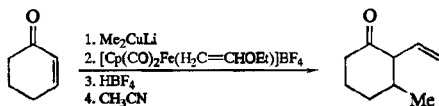
RM $\text{RCH}=\text{CHCu} \cdot n\text{-Bu}_3\text{P}$

JACS 110 4718 (1988)

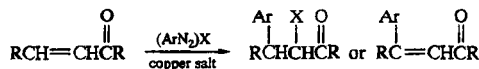
JOC 55 5528 (1990)

 $\text{Ph}_2\text{Cu}(\text{CN})\text{Li}_2$

JOC 59 332 (1994)

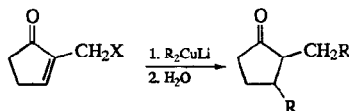


Org Syn Coll Vol 8 479 (1993)



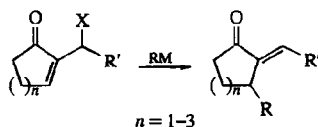
X = halogen

Org Rxs 11 189 (1960) (review); 24 225 (1976)



X = Cl, OAc, SPh

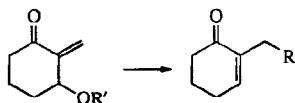
TL 21 3237 (1980)

 $n = 1-3$ X

OMe

 NR_2 RM $\text{RCu} \cdot 2n\text{-Bu}_3\text{P}$

TL 22 1809 (1981)

 R_2CuLi JOC 57 4895 (1992); 58 4471
(1993) (both chiral NR_2) R_2CuLi

TL 22 119 (1981)

CL 1189 (1981)

R_2CuMgX (R = vinylic)

CL 1189 (1981)

 $RCu(CN)ZnI$

TL 31 4481 (1990)



See page 351, Section 1; page 359, Section 2; page 362, Section 3; and page 392, Section 22.

XOrganocopper reagent

Cl

 R_2CuLi
 $CH_3CH(MgBr)CH_2CH_2CH=C(MgBr)CH_3$,
 cat $CuBr \cdot SMe_2$ (spiro product)

JOC 41 636 (1976)

TL 32 5861 (1991)

Cl, Br

 $[PhSCu(CH_2)_nCuSPh]Li_2$ ($n = 4, 5$; spiro
product)

TL 1245 (1977)

JACS 110 2218 (1988)

Cl, Br, I

 R_2CuLi

JOC 40 2694 (1975)

Can J Chem 60 1256 (1982)

I

 $RCu(CN)ZnI$, JEt_2

TL 29 6693 (1988)

OMs

 R_2CuLi

JOC 46 197 (1981)

OAc

 R_2CuLi

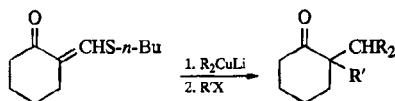
TL 2071 (1973)

SR

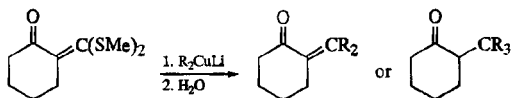
 R_2CuLi

CC 907 (1973)

JOC 52 110 (1987)

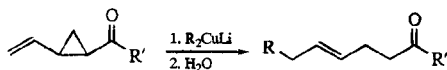


JOC 39 275 (1974)

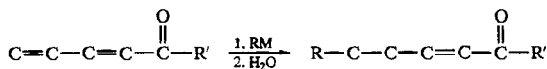


TL 3817 (1973)

Acta Chem Scand B 33 460 (1979)



Syn 317 (1975)

1M iMgX , cat CuCl

JACS 81 4069 (1959)

JOC 54 2317 (1989)

 iMgX , cat $\text{CuBr}\cdot\text{SMe}_2$

JCS Perkin I 2840 (1979)

 iMgX , cat $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$

Proc Chem Soc 356 (1962)

JOC 31 3109 (1966)

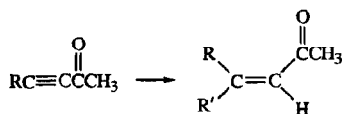
JACS 103 4466 (1981)

 i_2CuMgX , $\text{BF}_3\cdot\text{OEt}_2$

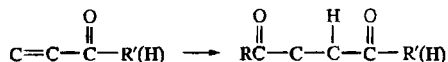
JOC 59 5983 (1994)

 i_2CuLi

TL 3795 (1971)



See page 421, Section 2.8 and page 452, Section 2.28.

 $\text{RCu}(\text{CN})\text{Li}$, $\text{CO}/\text{H}_2\text{O}$

TL 27 1473 (1986)

 $\text{R}_2\text{Cu}(\text{CN})\text{Li}_2$, $\text{CO}/\text{H}_2\text{O}$

JACS 107 4551 (1985)

 $\text{RCuMe}(\text{CN})\text{Li}_2$, $\text{CO}/\text{H}_2\text{O}$ (R = allylic)

TL 31 477 (1990)

 $n\text{-Bu}_3\text{SnCH}(\text{OEt})_2$, $n\text{-BuLi}/\text{CuI}/\text{H}_3\text{O}^+$ ($\text{R} = \text{H}$)

JOMC 2/2 C31 (1981)

 $[\text{RC}(\text{SPh})_2]_2\text{CuLi}/\text{H}_2\text{O}$, CuCl_2

JACS 94 8641 (1972)

 $(\text{H}_2\text{C}=\text{COR}')_2\text{CuLi}/\text{H}_3\text{O}^+$ ($\text{R}' = \text{Me}$, Et ; $\text{R} = \text{Me}$)

CC 519 (1975)

JACS 97 3822 (1975)

JOC 44 4781 (1979)

 $[\text{R}'\text{CH}=\text{CB}(\text{OR})_2]\text{Cu}(\text{CN})\text{ZnI}/\text{H}_2\text{O}_2$ ($\text{R} = \text{R}'\text{CH}_2$)

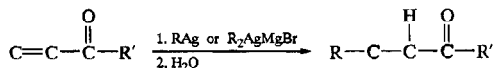
TL 33 3717 (1992)

 $(\text{R}'\text{CH}=\text{CSiMe}_3)_2\text{CuLi}/(\text{HOCH}_2)_2$, $\text{TsOH}/$

TL 3365 (1974)

 $m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}/\text{aq HClO}_4$ or

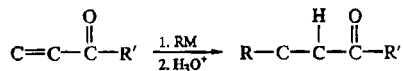
JOC 44 4781 (1979)

 $\text{BF}_3\cdot\text{OEt}_2\cdot\text{CH}_3\text{OH}$ ($\text{R} = \text{R}'\text{CH}_2$)**19. Organosilver Compounds**

TL 31 1553 (1990)

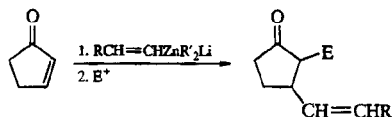
20. Organozinc Compounds

See also page 1596, Section 16; and page 1599, Section 18.



RM

3 RLi, ZnCl ₂ ·TMEDA	Ber 119 1581 (1986)
RMgX, various cat chiral Zn(II) complexes (enantioselective)	JOC 55 4168 (1990)
RMgCl, 2 MeLi, ZnCl ₂ ·TMEDA	JOC 53 4133 (1988)
2 RMgBr, ZnCl ₂ ·TMEDA, KO- <i>t</i> -Bu	TL 29 3593 (1988)
3 RMgX, ZnCl ₂ ·TMEDA	JOC 51 3993 (1986) Ber 119 1581 (1986)
RZnBr (R = 2°, 3° alkyl)	JACS 117 10775 (1995)
H ₂ C=C(SiMe ₃)CH ₂ ZnCl, cat BF ₃ ·OEt ₂	SL 279 (1993)
RC≡CZnBr, R ₃ SiOTf	TL 31 7627 (1990)
Me ₂ Zn, Me ₃ SiCl	JACS 114 1438 (1992)
Et ₂ Zn	Polymer J 9 595 (1977)
Et ₂ Zn, (cat) chiral β-aminoalcohol (enantioselective)	TL 32 95 (1991)
Ph ₂ Zn	JACS 63 2046 (1941)
R ₃ ZnLi	CL 679 (1977) Helv 62 1710 (1979) Ber 119 1581 (1986)
R ₃ ZnMgX	Ber 119 1581 (1986)
RZnMe ₂ Li	TL 27 1437 (1986)
RCH=CHZnMe ₂ Li	TL 31 7349 (1990); 33 5973 (1992)
PhMe ₂ SiZnMe ₂ Li	TL 36 5683 (1995)



E⁺

RC≡CCH₂I

SL 22 (1989)

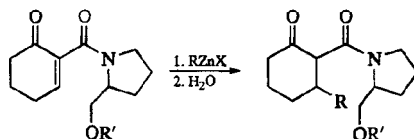
JOC 54 1785 (1989)

RCHO

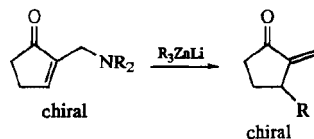
SL 22 (1989)
 JOC 55 1136 (1990)
 JACS 114 8008 (1992)

 $\text{H}_2\text{C}=\text{CRNO}_2$

SL 22 (1989)

R = Me (with or without Me_3SiCl), 1° alkyl, allyl, vinyl, aryl

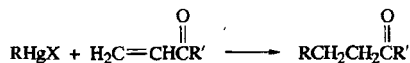
JACS 113 4926 (1991)



JOC 57 4895 (1992)

21. Organomercury Compounds

See also page 1598, Section 17.



Review: Chem Rev 88 487 (1988)

 NaBH_4

Angew Int 20 965, 967 (1981)
 TL 23 931 (1982)
 Syn 735 (1982)
 Ber 117 2132 (1984)
 Tetr 41 4025 (1985)

 NaHB(OMe)_3

TL 21 1829 (1980)
 JOC 47 2231 (1982) (intramolecular)
 Ber 117 2132 (1984)

 R_3SiH , DMSO

SL 701 (1993)
 JACS 117 3952 (1995)

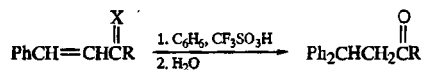
 $n\text{-Bu}_3\text{SnH}$

Ann 427 (1987)

 KI , $\text{K}_2\text{S}_2\text{O}_8$, $h\nu$

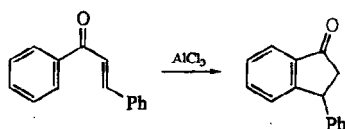
JOC 54 3768 (1989)
 SL 87 (1990)

22. Other Reagents

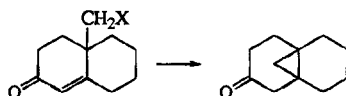


R = H, Me, Ph; X = O, NMe_2^+ , NOH

JACS 113 1364 (1991)



JOC 55 2060 (1990)



X = I, OTs, OMs

Li, NH₃

JACS 83 2783 (1961); 86 1432 (1964); 87 275 (1965); 105 5679 (1983)

Zn, HOAc

JACS 86 1432 (1964)

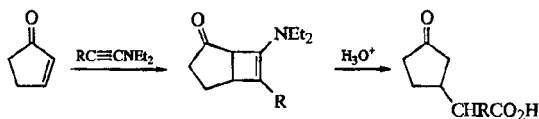
Me₂CuLi

TL 187 (1975)

Tetr 35 1183 (1979)

electrolysis

JOC 46 5455 (1981)



TL 23 1821 (1982)

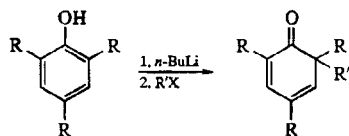


TL 31 2243 (1990)

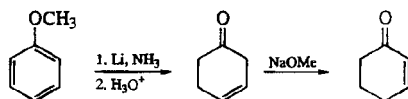


TL 34 441, 445 (1993); 35 4887 (1994); 36 4749 (1995)
SL 559 (1995)

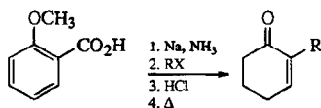
16. MISCELLANEOUS REACTIONS



JOC 54 6125 (1989)



TL 32 2621. (1991)

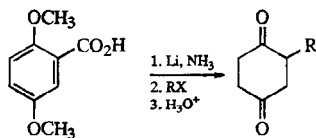


JOC 41 2649 (1976)

Org Syn 61 59 (1983)

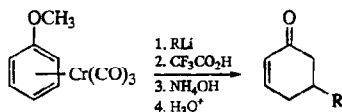
Org Syn Coll Vol 7 249 (1990)

TL 32 2621 (1991)

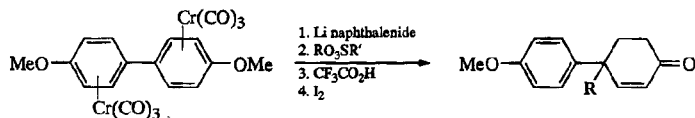


Syn 374 (1979)

JOC 45 1722 (1980); 52 2297 (1987)

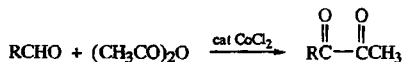


JOC 44 3275 (1979)

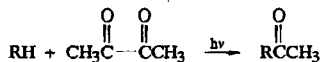
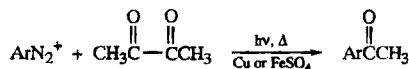


R = Me, Et, allyl

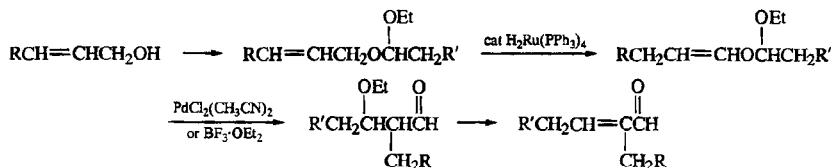
TL 29 5483 (1988)



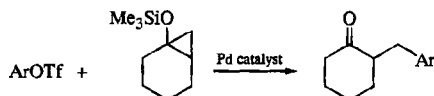
CC 692 (1987)

JOC 38 3447 (1973); 43 2370 (1978); 53 4369 (1988)
TL 2329 (1973)

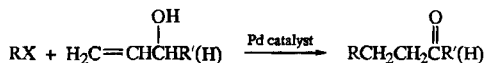
TL 23 1831 (1982)



CL 1361, 1435 (1981)

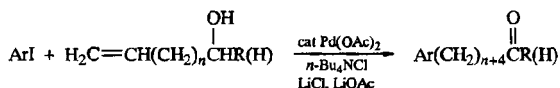


JACS 110 3296 (1988)

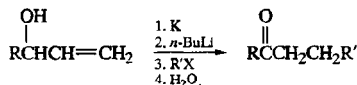


RX

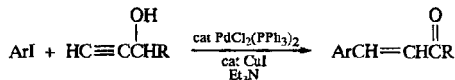
- ArX JOC 41 265, 273, 1206 (1976); 58 3731 (1993); 60 6970 (1995)
 Tetr 35 329 (1979)
 Syn Commun 11 579 (1981)
 TL 22 2479 (1981); 29 1283 (1988); 32 2121, 6113 (intramolecular) (1991); 36 6287 (1995)
 JACS 111 8932 (1989)
 SL 85 (1990)
 Org Syn Coll Vol 7 361 (1990)
- ArHgOAc JACS 90 5526 (1968)
 Org Syn Coll Vol 6 815 (1988) [stoichiometric Pd(OAc)₂]
- RCH=CHX TL 30 5737 (1989); 31 6641 (1990); 32 6113 (1991) (intramolecular)
 JACS 111 8932 (1989)
 SL 85 (1990); 349 (1992)
- RCH=CHOTf TL 34 4219 (1993) (intramolecular, chiral)
- RCH=CHHgX TL 30 5737 (1989) (stoichiometric Li₂PdCl₄)



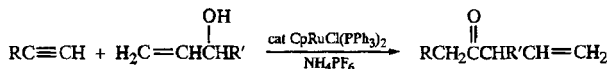
TL 30 6629 (1989); 34 7017 (1993); 35 5369 (1994)



TL 28 2587 (1987)



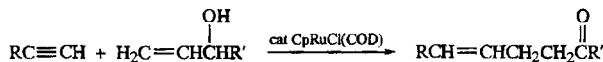
SL 115 (1991)



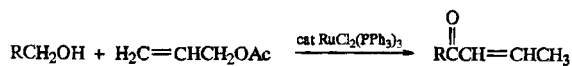
JACS 112 7809 (1990); 114 5579 (1992)

TL 34 587 (1993)

JOC 59 1078 (1994)



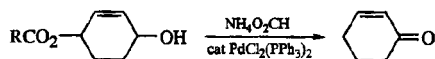
JACS 115 10402 (1993)



IOC 56 487 (1991)



TL 34 3207 (1993)

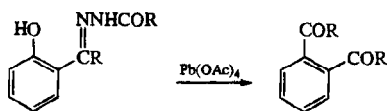


TL 34 8485 (1993)

CC 788 (1993)

Syn 948 (1993)

SL 601 (1993)



TL 28 4321 (1987); 35 6753 (1994)

Syn 1172 (1990)

IOC 56 5049 (1991)

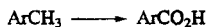
NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES

GENERAL REFERENCES

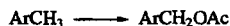
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed. Vol VIII (carboxylic acids and derivatives, nitriles), G. Thieme, Stuttgart (1952)
- "The Chemistry of Carboxylic Acids and Esters," Ed. S. Patai, Interscience, New York (1969)
- "The Chemistry of the Cyano Group," Ed. Z. Rappoport, Interscience, New York (1970)
- "The Chemistry of Amides," Ed. J. Zabicky, Interscience, New York (1970)
- "The Chemistry of Acyl Halides," Ed. S. Patai, Interscience, New York (1972)
- "Supplement B: The Chemistry of Acid Derivatives," Ed. S. Patai, Parts 1 and 2, J. Wiley, New York (1979)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E4 (acid derivatives), G. Thieme, Stuttgart-New York (1983)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E5 (acids and derivatives), Part 1, G. Thieme, Stuttgart-New York (1985)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E5 (acids and derivatives), Part 2, G. Thieme, Stuttgart-New York (1985)
- "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 6, Parts 2.1-2.3, pp 301-418
- M. A. Ogliaruso and J. F. Wolfe, "Synthesis of Carboxylic Acids, Esters, and Their Derivatives," Eds. S. Patai and Z. Rappoport, J. Wiley & Sons, New York (1991)
- "Organic Chemistry of β -Lactams," Ed. G. I. Georg, VCH, New York (1992)
- "The Chemistry of β -Lactams," Ed. M. I. Page, Blackie Academic and Professional/Chapman and Hall, London (1992)
- "Supplement B: The Chemistry of Acid Derivatives," Ed. S. Patai, Vol 2, Part 2, J. Wiley, Chichester, U. K. (1992)
- M. A. Ogliaruso and J. F. Wolfe, "Synthesis of Lactones and Lactams. Updates to the Chemistry of Functional Groups," J. Wiley & Sons, New York (1993)
- Syn 441 (1993) (Recent Advances in β -Lactone Chemistry)
- "Supplement B: The Chemistry of Acid Derivatives," Ed. S. Patai, Vol 2, Part 1, J. Wiley, Chichester, U. K. (1993)
- Contemporary Organic Synthesis 1 475 (1994)

1. OXIDATION, SUBSTITUTION AND ADDITION

1. Alkanes

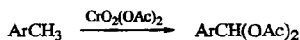


O_2 , KO- <i>t</i> -Bu, DMF	JOC 28 410 (1963)
NaOCl, cat $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, cat <i>n</i> -Bu ₄ NBr	JOC 51 2880 (1986)
HNO_3	Org Syn Coll Vol 3 820, 822 (1955)
SeO_2 , K_2CO_3	SL 422 (1992) (Ar = pyridine)
PbO_2 , KOH	Org Syn Coll Vol 5 617 (1973)
<i>t</i> -BuO ₂ H, cat Cr-pillared montmorillonite	JOC 57 5841 (1992)
CrO_3 , HOAc	JACS 78 1689 (1956)
$\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4	Org Syn Coll Vol 1 392, 543 (1941) JOC 23 1236 (1958)
$\text{Na}_2\text{Cr}_2\text{O}_7$ / HCl	Org Syn Coll Vol 5 810 (1973)
KMnO ₄	Org Syn Coll Vol 1 159 (1941); 2 135 (1943); 3 740 (1955) JOC 53 3513 (1988) TL 35 5169 (1994)
(<i>n</i> -Bu ₄ N)MnO ₄ , py	CC 253 (1978)

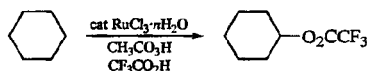


$\text{Na}_2\text{S}_2\text{O}_8$, Cu(OAc) ₂	Syn 477 (1980)
$\text{K}_2\text{S}_2\text{O}_8$, Cu(OAc) ₂	JCS Perkin I 669 (1979)
Pb(OAc) ₄	JCS 143 (1945); 3943 (1954) JACS 91 138 (1969) Syn 567 (1973) (review) JOC 58 7548 (1993)

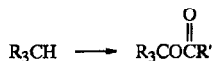
Mn(OAc) ₃	JACS 91 138 (1969)
Co(OAc) ₃	JACS 91 6830 (1969)
Pd(OAc) ₂	Syn 567 (1973) (review)
Hg(OAc) ₂	JOC 50 3070 (1985)
CAN, HOAc	JOC 31 2033 (1966); 42 3682 (1977)
DDQ, HOAc	TL 28 5403 (1987)



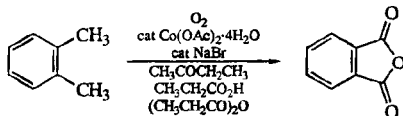
Syn 567 (1973) (review)



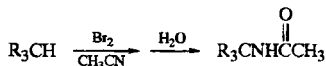
TL 35 7953 (1994)



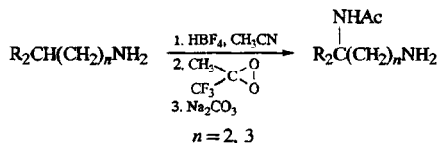
Pb(OAc) ₄ , LiCl, CF ₃ CO ₂ H	JCS Perkin I 2576 (1976) JOC 50 2759 (1985); 53 1102 (1988) JACS 110 1303, 8591 (1988)
CrO ₃ , Ac ₂ O, HOAc	JOC 50 2759 (1985)
Pd(O ₂ CCF ₃) ₂	JACS 109 8109 (1987)



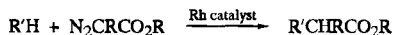
SL 495 (1992)



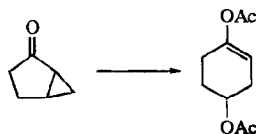
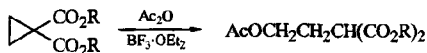
Syn 632 (1977)



JACS 115 7250 (1993)



See page 1724, Section 2.



JOC 53 440 (1988)

2. Arenes

(RCO₂)₂; O₂, I₂, CuCl₂ or Lewis acid

Syn 1 (1972) (review)

Me₃SiOAc, PhI(O₂CCF₃)₂

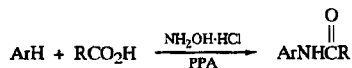
JACS 116 3684 (1994)

Pb(OAc)₄

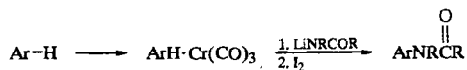
Syn 567 (1973) (review)

K₂S₂O₈, cat Pd(O₂CCF₃)₂

JACS 109 8109 (1987)



JOC 59 5814 (1994)



TL 30 3373 (1989)

O₃/H₂O₂

BCSJ 39 1075 (1966)

JOC 42 1254 (1977)

JACS 98 122 (1976); 108 2343 (1986); 109 5524 (1987); 112 3156 (1990)

NaOCl, cat RuO₂·nH₂O, HCl

JACS 110 5479 (1988)

NaIO₄, cat RuO₂

JOC 58 1372, 2286 (1993)

NaIO₄, RuO₄

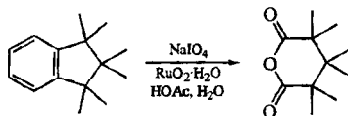
JACS 110 4035 (1988)

NaIO₄, cat RuCl₃·H₂O

JOC 46 3936 (1981); 48 712, 2346 (1983); 53 3178 (1988); 55 1928 (1990); 57 4567 (1992); 58 2953 (1993)

KMnO₄, KOH, n-Hex₄NBr

JACS 110 900 (1988)



JOC 53 4626 (1988)

3. Alkenes

For alkenol \rightarrow lactone, see page 1861, Section 8. For the addition of HCN to alkenes, see page 1705, Section 9. See also page 638, Section 4; and page 1641, Section 11.



Review: BSCF 65 (1986)

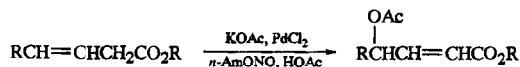
$\text{Pb}(\text{OAc})_4$	Ann 481 263 (1930) JOC 29 3353 (1964) Syn 567 (1973) (review)
$\text{Mn}(\text{OAc})_3$, cat KBr	JCS C 2355 (1971)
$\text{Hg}(\text{OAc})_2$	JCS 2381 (1951) JOC 29 3353 (1964) TL 3719 (1965); 4203 (1966); 3483 (1970) JACS 94 2320 (1972) Syn 567 (1973) (review) R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer, New York (1986), pp 190-196
cat PdCl_2 , CuCl_2 , HOAc, NaOAc, (PPh_3)	Angew Int 21 366 (1982)
cat $\text{Pd}(\text{OAc})_2$, cat hydroquinone, cat Fe or Co, O_2 , HOAc	JACS 112 5160 (1990)
cat $\text{Pd}(\text{OAc})_2$, cat hydroquinone, cat $\text{Cu}(\text{OAc})_2$, O_2 , HOAc	JOC 55 5674 (1990)
cat $\text{Pd}(\text{OAc})_2$, cat benzoquinone, H_2O_2 or $t\text{-BuO}_2\text{H}$, RCO_2H	JOC 59 5729 (1994)
cat $\text{Pd}(\text{OAc})_2$, cat benzoquinone, MnO_2 , HOAc	Angew Int 23 453 (1984) JOC 55 975 (1990) Org Syn Coll Vol 8 137 (1993)
cat $\text{Pd}(\text{OAc})_2$, cat $\text{Fe}(\text{NO}_3)_3$, O_2 , HOAc	TL 34 2523 (1993)
RCO_2H , cat $t\text{-BuO}_2\text{H}$, cat Cu_2Cl_2	JOC 59 2848 (1994)
$t\text{-C}_4\text{H}_9\text{O}_3\text{CC}_6\text{H}_5$, Cu(I) or Cu(II)	JACS 80 756 (1958); 81 5819 (1959); 84 774, 4969 (1962); 86 3753 (1964); 108 8230 (1986) Org Syn 48 18 (1968) Syn 1 (1972) (review) TL 28 1561 (1987)

t-C₄H₉O₃CC₆H₅, cat CuOTf, cat chiral
bis(oxazoline) (enantioselective)

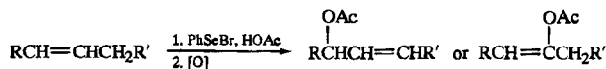
TL 36 1831, 2945 (1995)

t-C₄H₉O₃CC₆H₅, cat Cu(OTf)₂, cat chiral
tris(oxazoline) (enantioselective)

SL 1245 (1995)



TL 22 131 (1981)



JACS 106 1446 (1984)

JOC 54 884 (1989)



TsN=S=NTs

JOC 41 176 (1976)

TsN=Se=NTs

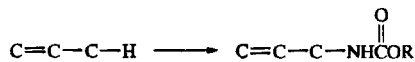
JACS 98 269 (1976); 112 462 (1990) (enol silane);
113 672 (1991) (enol silane)

PhI=NTs, cat Mn porphyrins

TL 29 1927 (1988)

PhSO₂NSO/(Me₃Si)₂NH/NaOH

Tetr 44 4243 (1994)



EtO₂CN=NCO₂Et, SnCl₄/Li, NH₃

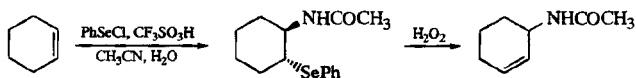
JOC 58 5261 (1993)

MeO₂CN=S=NCO₂Me/KOH, MeOH

JOC 48 3561 (1983)
Org Syn 65 159 (1987)

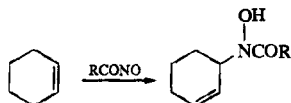
RO₂CNSO, SnCl₄/(Me₃Si)₂NH/LiOH

JACS 113 3526 (1991)

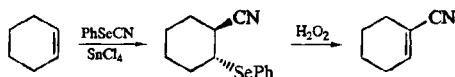


CC 546 (1981)

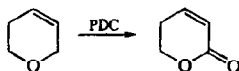
JOC 46 4727 (1981)



Tetr 37 4007 (1981)



CC 871 (1982)



JACS 110 7419 (1988)

BH₃/HOAc, NaOAc, electrolysis

CL 1021 (1974)

BH₃/Pb(OAc)₄ or PhI(OAc)₂

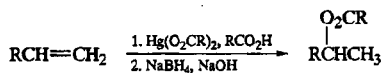
BCSJ 51 901 (1978)

BH₃/Hg(OAc)₂/I₂

JOC 39 834 (1974)

LiAlH₄, TiCl₄/Pb(OAc)₄

TL 1405 (1979)

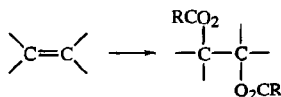


R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 5 (review)

TL 33 4865 (1992)



See page 991, Section 1.

I₂, AgO₂CR

Org Rxns 9 332 (1957) (review)

Adv Org Chem 1 117 (1960) (review)

JCS C 1327 (1966)

JOC 50 3070 (1985); 52 2226, 5574 (1987); 58 7283 (1993)

TL 29 3513 (1988)

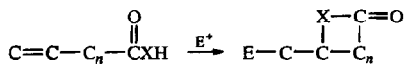
(PhIOiPh)(BF₄)₂, HOAc

TL 29 3717 (1988)

JOC 54 2609 (1989)

(PhIOiPh)X₂ (X = SbF₆, PF₆), HOAc

JOC 54 2609 (1989)



X = O, NR

See page 1861, Section 8.



H_2SO_4 , $\text{R}'\text{CN}/\text{H}_2\text{O}$

JACS 70 4045 (1948)

Org Rxs 17 213 (1969) (review)

SL 715 (1991)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 6, Part 1.9, p 261 (review)

 $\text{Hg}(\text{NO}_3)_2$, $\text{R}'\text{CN}/\text{NaBH}_4$, NaOH

JACS 91 5647 (1969)

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)

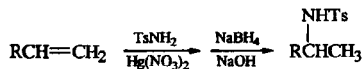
 $\text{Hg}(\text{BF}_4)_2$, $\text{R}'\text{CN}/\text{NaBH}_4$, NaOH

TL 33 4863 (1992)

 $\text{Hg}(\text{NO}_3)_2$, $\text{R}'\text{CONH}_2/\text{NaBH}_4$, NaOH, $n\text{-BuNH}_2$
($\text{R}' = \text{Me}$, Ph, NH_2 , OEt)

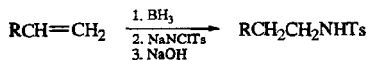
CC 670 (1981)

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)

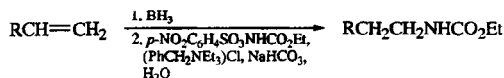


CC 1178 (1981)

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)



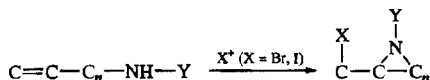
TL 181 (1978)



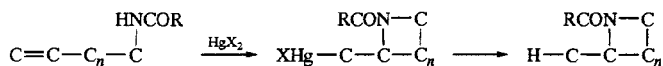
Syn Commun 11 475 (1981)

 $\text{X} = \text{COR}$, CO_2R , SO_2Ar

See page 761, Section 3.

 $n = 3, 4$ $\text{Y} = \text{CO}_2\text{Me}$, $p\text{-MeC}_6\text{H}_4\text{SO}_2$

Heterocycles 23 192 (1985)



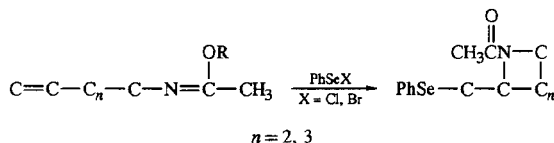
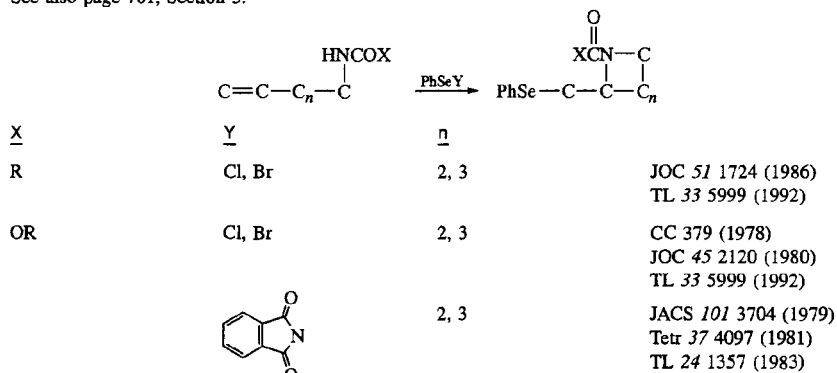
X = OAc, O₂CCF₃, NO₃; n = 2, 3

R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 7 (review)

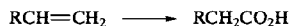
JOC 52 4717 (1987)

TL 30 1777, 4775 (R = OR), 7321 (1989); 31 6765 (1990)

See also page 761, Section 3.



JCS Perkin I 1837 (1986)

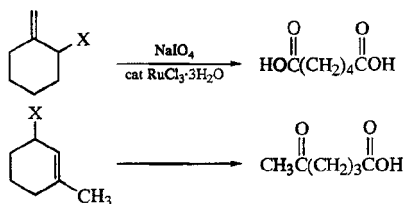


BH ₃ /CrO ₃	CC 122 (1968)
BH ₃ ·SMe ₂ or H ₂ BCl·SMe ₂ or HBBBr ₂ ·SMe ₂ or Me ₂ CHCMe ₂ BH ₂ or Cy ₂ BH/PDC or Na ₂ Cr ₂ O ₇ ·H ₂ SO ₄ or CrO ₃ ·HOAc·H ₂ O	JOC 57 6173 (1992)
Me ₂ CHCMe ₂ BH ₂ /CrO ₃ , HOAc, H ₂ O	JOC 59 365 (1994)
H ₂ BCl·SMe ₂ /CrO ₃ , HOAc, H ₂ O	JOC 59 365 (1994)
Br ₂ BH/H ₂ O/CrO ₃ , HOAc, H ₂ O	TL 33 1037 (1992)
(Sia) ₂ BH/CrO ₃ , HOAc, H ₂ O	JOC 59 365 (1994)



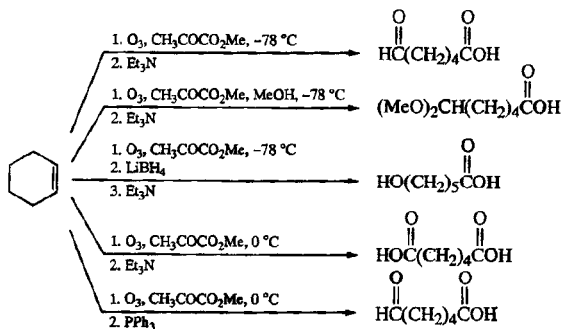
O ₃ /H ₂ O ₂	Chem Rev 27 437 (1940); 58 925 (1958) (reviews)
O ₃ /K ₂ Cr ₂ O ₇ , H ₂ SO ₄	JACS 108 4603 (1986)

O_3/H_2 , Lindlar catalyst	Bull Acad Sci USSR, Div Chem Sci 25 1790 (1976) JOC USSR 14 48 (1978)
$NaOCl$, cat $RuCl_3$	CC 1420 (1970) JOC 46 3936 (1981) JACS 103 464 (1981) TL 28 3061, 5441, 6331 (1987)
H_5IO_6 , cat $RuCl_3 \cdot H_2O$	JOC 55 1928 (1990)
$NaIO_4$, cat $RuCl_3 \cdot 3H_2O$	JOC 56 1453 (1991); 58 255 (1993) JACS 114 671 (1992)
$NaIO_4$, cat RuO_4	JACS 85 3419 (1963)
$NaIO_4$, cat $KMnO_4$	Can J Chem 33 1701 (1955); 34 1413 (1956) JACS 107 7967 (1985)
H_2CrO_4 , cat OsO_4	JOC 58 4745 (1993)
$NaMnO_4$, <i>t</i> -BuOH, H_2O	JOC 26 3734 (1961)
$KMnO_4$, acetone	JOC 58 6126 (1993)
$KMnO_4$, H_2O	Org Syn Coll Vol 2 53 (1943)
$KMnO_4$, H_2O , CO_2	JOC 53 929 (1988)
$KMnO_4$, Na_2CO_3 , <i>t</i> -BuOH, acetone	JACS 108 468 (1986)
$KMnO_4$, KNO_3 , K_2CO_3	JOC 26 3734 (1961)
$KMnO_4$, R_4NCl (phase transfer)	TL 1511 (1974) JOC 42 3749 (1977) Org Syn 60 11 (1981)
$KMnO_4$, dimethyl polyethylene glycol	JOC 43 1532 (1978)
$KMnO_4$, $CuSO_4 \cdot 5H_2O$	JOC 54 5182 (1989)
$(n-Bu_4N)MnO_4$, py	CC 253 (1978)

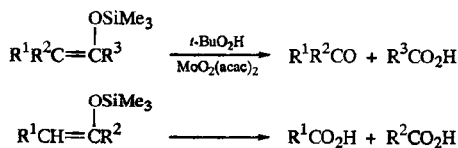


X = H, OH

JOC 52 689 (1987)



TL 34 6591 (1993)



TL 22 2595 (1981)

 $\text{O}_3/\text{R}'\text{OH}$, HCl

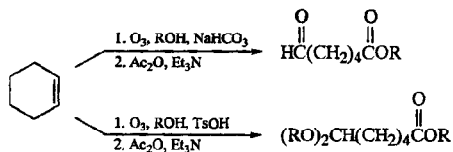
Angew Int 17 939 (1978)

 O_3 , NaOH , $\text{R}'\text{OH}$

SL 643, 1007 (1992)

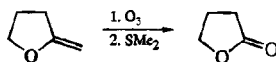
JOC 58 3675 (1993)

TL 34 6619 (1993)



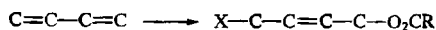
TL 23 3867 (1982)

Org Syn Coll Vol 7 168 (1990)



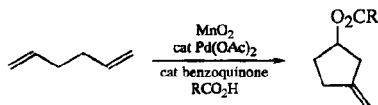
TL 34 5807 (1993)

4. Dienes

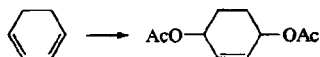


X = halogen

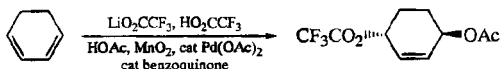
See page 638, Section 4.



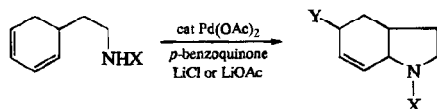
JOC 54 4914 (1989); 57 6579 (1992)

**Stereochemistry****Reagents**

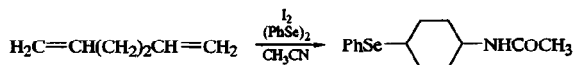
cis	HOAc, LiOAc, cat $\text{Pd}(\text{OAc})_2$, benzoquinone	JOC 54 3882 (1989)
	HOAc, LiOAc, LiCl, cat $\text{Pd}(\text{OAc})_2$, benzoquinone	JACS 103 4959 (1981)
	HOAc, LiOAc, MnO_2 , cat $\text{Pd}(\text{OAc})_2$, cat benzoquinone	JOC 60 615 (1995)
	HOAc, LiOAc, LiCl, MnO_2 , cat $\text{Pd}(\text{OAc})_2$, cat benzoquinone	JOC 49 4619 (1984); 58 7185 (1993)
	HOAc, LiOAc, LiClO_4 , LiCl, cat $\text{Pd}(\text{OAc})_2$, cat hydroquinone, electrolysis	CC 1236 (1987)
	HOAc, LiOAc, cat $\text{Pd}(\text{OAc})_2$, cat hydroquinone, Co or Fe catalyst, O_2	JACS 112 5160 (1990)
trans	HOAc, LiOAc, cat $\text{Pd}(\text{OAc})_2$, benzoquinone	JACS 103 4959 (1981)
	HOAc, LiOAc, MnO_2 , cat $\text{Pd}(\text{OAc})_2$, cat benzoquinone	JOC 49 4619 (1984)
	HOAc, LiOAc, LiClO_4 , cat $\text{Pd}(\text{OAc})_2$, cat hydroquinone, electrolysis	CC 1236 (1987)
	HOAc, LiOAc, cat $\text{Pd}(\text{OAc})_2$, cat hydroquinone, cat Co(II) <i>meso</i> -tetraphenylporphyrin, O_2	JACS 109 4750 (1987); 112 5160 (1990)
	HOAc; LiOAc; cat $\text{Pd}(\text{OAc})_2$; cat hydroquinone; Co, Mn or Fe catalyst; O_2	JACS 112 5160 (1990)
	HOAc, LiOAc, cat $\text{Pd}(\text{OAc})_2$, cat (phenyl- sulfinyl)benzoquinone, cat iron phthalocyanine, O_2	JOC 56 5808 (1991)



TL 25 2717 (1984)

X = Ts, Ac, CO_2R ; Y = Cl, OAc

JACS 112 3683 (1990)



CC 87 (1982)

5. Alkynes



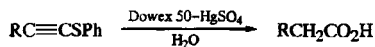
H_2O_2 , cat $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, cat $\text{Hg}(\text{OAc})_2$, cat hexaethylphosphoric triamide	JOC 53 830 (1988)
H_2O_2 , cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PMo}_{12}\text{O}_{40}$, cat $\text{Hg}(\text{O}_2\text{CCF}_3)_2$	JOC 54 947 (1989)
H_2O_2 , cat $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, cat $\text{Hg}(\text{OAc})_2$, cat phase transfer agent	JOC 53 830 (1988)
H_2O_2 , cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PW}_{12}\text{O}_{40}$, cat $\text{Hg}(\text{O}_2\text{CCF}_3)_2$	JOC 54 947 (1989)
H_2O_2 , cat MeReO_3	JOC 60 7728 (1995)
$\text{C}_6\text{F}_5\text{I}(\text{O}_2\text{CCF}_3)_2$, H_2O , C_6H_6	JOC 53 6124 (1988)
PhIO , cat $\text{RuCl}_2(\text{PPh}_3)_3$	Helv 64 2531 (1981)
NaIO_4 , cat RuCl_3	JOC 55 6289 (1990)
NaIO_4 or NaOCl , cat RuO_2	TL 2941 (1971)
NaIO_4 , cat OsO_4	JOC 60 650 (1995)
KMnO_4 , HOAc , H_2O , Aliquat 336	JOC 42 3749 (1977)
KMnO_4 , HOAc , H_2O , Adogen-464	Syn 462 (1978)
$\text{Ti}(\text{NO}_3)_3$	IACS 93 7331 (1971); 95 1296 (1973)



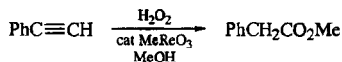
O_3	Chem Rev 27 437 (1940) (review)
H_2O_2 , cat $[\text{C}_5\text{H}_5\text{N}(\text{CH}_2)_{15}\text{CH}_3]_3\text{PM}_{12}\text{O}_{40}$ ($\text{M} = \text{Mo}, \text{W}$), cat $\text{Hg}(\text{O}_2\text{CCF}_3)_2$	JOC 54 947 (1989)
$\text{C}_6\text{F}_5\text{I}(\text{O}_2\text{CCF}_3)_2$, H_2O , C_6H_6	JOC 53 6124 (1988)
NaIO_4 , cat RuO_2	SL 165 (1994)
KMnO_4 , H_2O	JOC 44 2726 (1979)



H_2O_2 , cat MeReO_3	JOC 60 7728 (1995)
$\text{BH}_3/m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$	JACS 89 291 (1967)
$n\text{-BuLi}/\text{Me}_3\text{SiCl}/\text{Cy}_2\text{BH}/\text{H}_2\text{O}_2$, NaOH	JACS 99 3184 (1977); 106 6006 (1984) JOC 56 3549 (1991); 59 1139 (1994)



TL 33 4911 (1992)



JOC 60 7728 (1995)

 $\text{H}_2\text{O}, \text{H}_2\text{SO}_4$

SL 502 (1992)

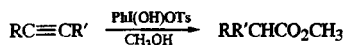
 $\text{EtOH}, \text{ZnCl}_2$

TL 36 7023 (1995)

 $\text{EtOH}, \text{cat HgCl}_2$

JOC 54 9 (1988)

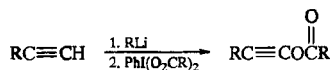
JACS 112 5583 (1990)



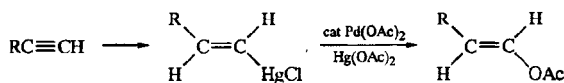
TL 28 2845 (1987)

 $\text{X} = \text{SiMe}_3, \text{OR}, \text{NR}_2; \text{Y} = \text{OH}, \text{OR}, \text{NR}_2$

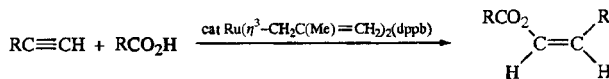
See page 1217, Section 6.



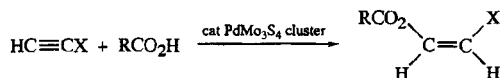
JACS 110 3272 (1988)



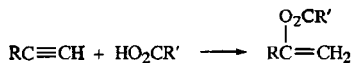
JACS 102 1966 (1980)



CC 850 (1993)

 $\text{X} = \text{COR}, \text{CO}_2\text{R}, \text{CONR}_2, \text{SO}_2\text{Ar}$

TL 36 5585 (1995)

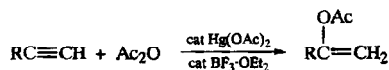


Review: JACS 102 1966 (1980)

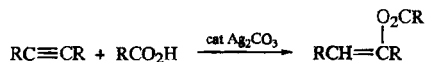
Catalyst

$[\text{Ru}(\text{CO})_2(\text{OAc})]_n$	Organomet 2 1689 (1983)
$[\text{Ru}(\text{CO})_2(\text{O}_2\text{CH})(\text{PPh}_3)]_2$	SL 707 (1995)
$\text{Ru}_3(\text{CO})_{12}$	Organomet 2 1689 (1983) JOMC 448 189 (1993)
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}, (\text{PR}_3)$	TL 27 6323 (1986)
$\text{RuCl}_2(\text{PR}_3)(p\text{-cymene})$	TL 27 6323 (1986) (R = Me); 29 5365 (1988) (R = Ph); 32 5359 (1991) JCS Perkin I 1197 (1991) SL 755 (1991) (review); 273 (1993) (R = OEt)
bis(η^5 -cyclooctadienyl)ruthenium, cat PR_3 , (cat maleic anhydride)	JOC 50 1566 (1985); 52 2230 (1987) TL 27 2125, 5389 (1986)
$\text{Ru}(\eta^1\text{-methallyl})_2(\text{dppb})$	JOC 60 7247 (1995)
$\text{PdCl}_2(\text{PhCN})_2, \text{Et}_3\text{N}$	TL 25 5323 (1984) (intramolecular)
$\text{Hg}(\text{OAc})_2$	JACS 77 939 (1955); 103 5459 (1981) (intramolecular)
$\text{HgO} \cdot \text{BF}_3 \cdot \text{OEt}_2 \cdot \text{MeOH}$	JACS 56 1802 (1934)

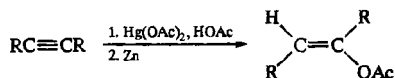
For intramolecular reactions, see page 1861, Section 8.



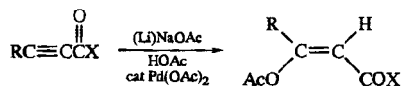
JOC 38 4254 (1973)



CL 645 (1981)



JOC 47 3707 (1982)

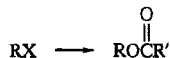


X = OR, NH_2

TL 33 7205 (1992)

6. Alkyl Halides

See also page 1932, Section 3.



$\text{NaO}_2\text{CR}'$, HMPA ($\text{RX} = 1^\circ \text{RBr}$; 1°RI ; allylic Cl ; benzylic Cl) JOC 39 3721 (1974)

$\text{KO}_2\text{CR}'$, alumina ($\text{RX} = 1^\circ$, 2°RBr ; $1^\circ \text{R}_2\text{SO}_4$) Syn Commun 10 279 (1980)

KOAc , alumina or silica, microwave irradiation ($\text{RX} = 1^\circ \text{RBr}$) TL 30 945 (1989)

KOAc , cat $[(n\text{-C}_8\text{H}_{17})_3\text{N}(n\text{-Pr})]\text{Cl}$ ($\text{RX} = 1^\circ \text{RBr}$, 2° allylic Br) Syn 867 (1974)

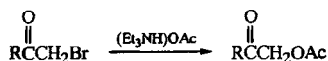
$\text{CsO}_2\text{CR}'$, DMF ($\text{RX} = 2^\circ \text{RBr}$; 1°RI ; 1° , 2°ROMs) JOC 46 4321 (1981)

$\text{Hg}(\text{O}_2\text{CR}')_2$, cat $\text{B}(\text{O}_2\text{CR}')_3$ [$\text{RX} = 1^\circ \text{RI}$; 3°RX ($\text{X} = \text{Cl}$, Br , I); $\text{H}_2\text{C}=\text{CHCH}_2\text{X}$ ($\text{X} = \text{Cl}$, Br , I), PhCH_2X ($\text{X} = \text{Cl}$, Br , I)] JOC 39 3721 (1975)

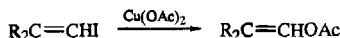
AgO_2CCF_3 , $\text{CF}_3\text{CO}_2\text{H}$ ($\text{RX} = 3^\circ \text{RCl}$) JACS 110 1303 (1988)

$\text{R}'\text{CO}_2\text{H}$ ($\text{RX} = 3^\circ \text{RI}$) TL 27 6055 (1986)

$\text{PhI}(\text{OAc})_2$ ($\text{RX} = 3^\circ \text{RI}$) TL 27 6055 (1986)



TL 31 3669 (1990)



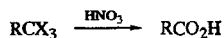
JOMC 93 415 (1975)



H_2SO_4 , $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ TL 36 5805 (1995)

$(\text{NO}_2)\text{BF}_4$, $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ JOC 45 165 (1980)

AgOTf , $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ JACS 110 1303, 8591 (1988)



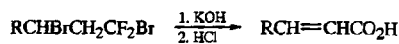
X

Cl

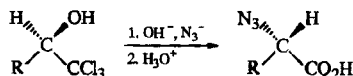
Dokl Akad Nauk SSSR 100 85 (1955)
J Gen Chem USSR 27 2481 (1957)

Br

JOC 58 3772 (1993)



JOC 54 3992 (1989)



JACS 114 1906 (1992)

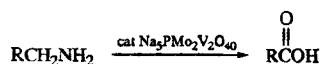
7. Amines

2,4,6-triphenylpyrylium perchlorate / R'CO₂Na

CC 701 (1977)

R'COCl / N₂O₄ / Δ

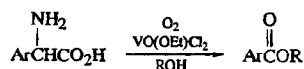
Org Syn Coll Vol 5 336 (1973)



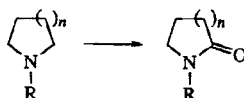
JOC 56 5707 (1991)



JACS 110 7230 (1988)



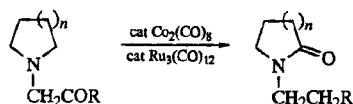
TL 31 3917 (1990)

 $n = 1, 2$ (PhIO)_n, H₂O

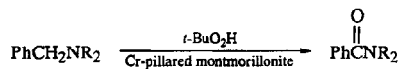
TL 29 6913 (1988)

Hg(OAc)₂, Na₂EDTA·2H₂O

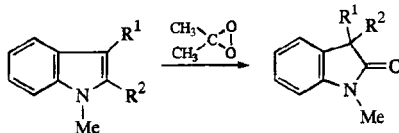
Syn Commun 18 1331 (1988)

 $n = 1-3$

JACS 114 7018 (1992)

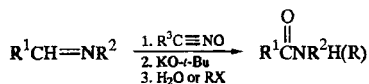


JOC 57 5841 (1992)



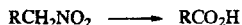
JACS 115 8867 (1993)

8. Imines



SL 189 (1991)

9. Nitro Compounds

 H_3O^+

Can J Chem 49 3483, 3489, 3493 (1971)

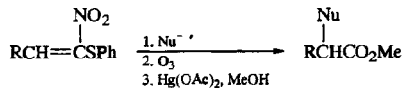
 KMnO_4 , KOH , K_2HPO_4 , $t\text{-BuOH}$

SL 591 (1991)

 $\text{LDA} / \text{MoO}_5 \cdot \text{py} \cdot \text{HMPA}$

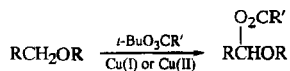
TL 22 5235 (1981)

10. Nitrothioalkenes

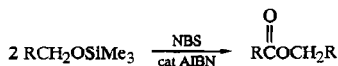
 $\text{Nu}^- = \text{KOSiMe}_3 (\text{OH}), \text{NaOR}, \text{KNHTs}, \text{imides}$

JACS 113 9820 (1991)

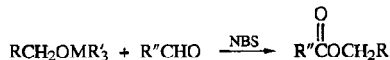
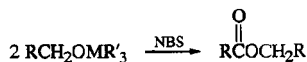
11. Ethers



Syn 1 (1972) (review)



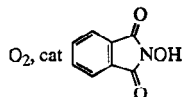
SL 345 (1990)

R₃MMe₃Si

JOC 43 371 (1978)

n-Bu₃Sn

JACS 98 1629 (1976)



JOC 60 3934 (1995)

O₂, cat Pt

JACS 114 6385 (1992)

CrO₃, HOAc

Helv 42 1124 (1959)
 CC 752 (1966) (Me > RCH₂)
 Carbohydr Res 12 147 (1970)
 JACS 107 5289 (1985)

H₂CrO₄

JCS 221, 227 (1959)

(PhCH₂NMe₃)MnO₄

TL 35 5567 (1994)

(PhCH₂NEt₃)MnO₄

Angew Int 18 69 (1979)

Zn(MnO₄)₂, silica gel

JACS 105 7755 (1983)

RuO₄

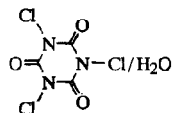
JACS 80 6682 (1958)
 JOC 28 2729 (1963); 58 4567 (1993)
 TL 28 435 (1987)

NaIO₄, cat RuO₂

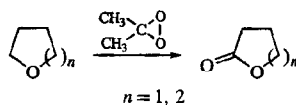
Syn Commun 10 205 (1980)
 JACS 102 3904 (1980); 107 1308 (1985)
 JOC 52 83 (1987); 60 169 (1995)

NaIO₄, cat RuCl₃·H₂O

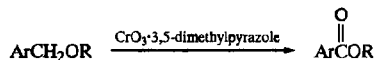
JOC 46 3936 (1981); 51 1015 (1986); 58 7498 (1993)
 JACS 112 9001 (1990)
 TL 35 5841 (1994)



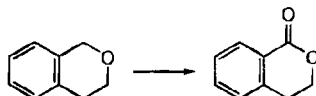
TL 5819 (1968)
 Tetr 27 2671 (1971)



TL 33 4225 (1992)



JACS 112 6959 (1990)

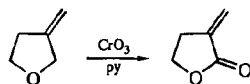


O₂, hv, cat FeCl₂, cat 9,10-dicyanoanthracene,
cat methylviologen

TL 32 4291 (1991)

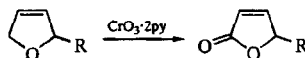
PCC

JOC 49 1647 (1984)

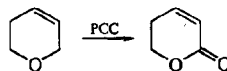


JOC 55 1096 (1990)

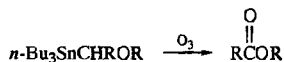
TL 36 2661 (1995)



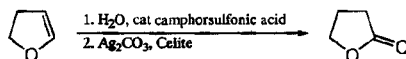
TL 28 5819 (1987)



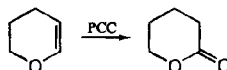
JOC 49 1647 (1984)



TL 35 5993 (1994)

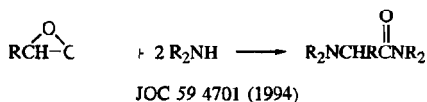
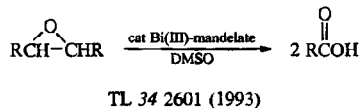
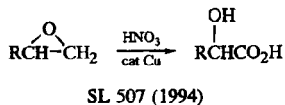
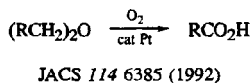
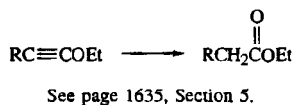
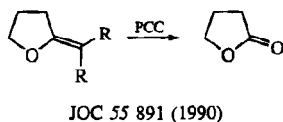
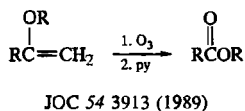
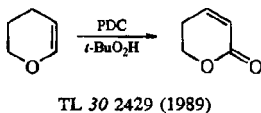
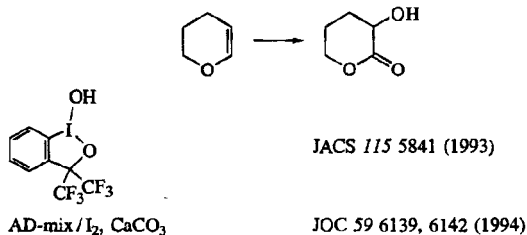


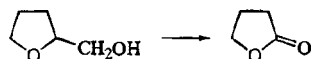
JOC 53 860 (1988)



Carbohydr Res 98 139 (1981)

TL 27 4011 (1986)





PCC TL 31 1509, 2775 (1990)

PDC, Ac₂O TL 33 3141 (1992)

KMnO₄, CuSO₄ TL 34 1979 (1993)



JOC 60 8267 (1995)



Ac₂O, NaI TL 28 2537 (1987)

Ac₂O, BF₃·OEt₂ JOC 57 3214 (1992)

Ac₂O, Me₃SiCl (R' = CH₃, CH₂SCCH₃) TL 24 1189 (1983)

Ac₂O, FeCl₃ JOC 39 3728 (1974); 59 4154 (1994)

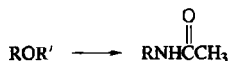
TL 24 3165 (1983); 29 2357, 2951, 6243 (1988)
SL 633 (1992)

R''COCl, NaI TL 23 681 (1982); 28 2537 (1987)

AcBr (R' = SiMe₃) TL 35 2027 (1994)

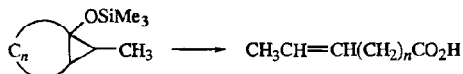
AcBr, cat SnBr₂ (R' = SiMe₃) TL 35 2027 (1994)

AcBr, cat SnBr₂ (R' = PhCH₂, *p*-MeOC₆H₄CH₂,
H₂C=CHCH₂) SL 437 (1993)



H₂SO₄, CH₃CN/H₂O TL 30 2967 (1989)

(NO₂)BF₄, CH₃CN/H₂O JOC 45 165 (1980)



Reagent

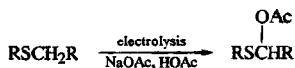
n

PhI(OAc)₂ 4–6 TL 36 6907 (1995)

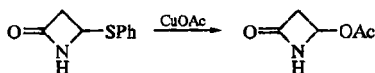
Pb(OAc)₄ 3–5 TL 4013 (1977)

JACS 107 4230 (1985)

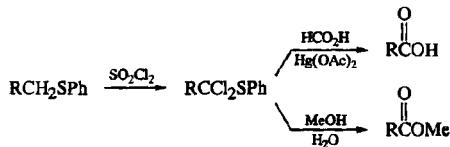
12. Sulfides



JOC 57 2946 (1992)



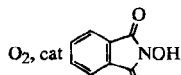
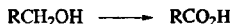
TL 35 5887 (1994)



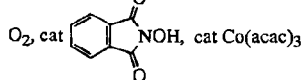
CC 857 (1982)

13. Alcohols

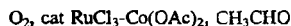
For alcohol \rightarrow ester, see also page 1929, Section 9. For alkenol \rightarrow lactone, see page 1861, Section 8.



JOC 60 3934 (1995)



TL 36 6923 (1995)



JOC 58 7318 (1993)



Ber 89 1648 (1956)

Tetr 9 67 (1960)

JACS 106 1095 (1984)

JOC 52 4898 (1987); 54 1866 (1989); 57 5247

(1992); 59 394 (1994)

TL 33 4313 (1992)



"Hydrogen Peroxide in Organic Chemistry," DuPont
(1962), p 57



JOC 56 5924 (1991)



JOC 53 3553 (1988)

nickel peroxide, NaOH	JOC 27 1597 (1962)
CH ₃ CO ₃ H, cat Ru-C	SL 733 (1995)
HNO ₃	Org Syn Coll Vol I 168 (1941) JOC 60 4666 (1995)
HNO ₃ , ultrasound	TL 31 4129 (1990)
CrO ₃ , HOAc	JACS 78 2255 (1956)
CrO ₃ , H ₂ SO ₄	JOC 48 4404 (1983)
K ₂ Cr ₂ O ₇ , H ₂ SO ₄	JACS 82 2498 (1960)
(C ₅ H ₅ NH) ₂ Cr ₂ O ₇ (PDC), DMF (non-allylic)	TL 399 (1979); 28 5311, 6069 (1987) JACS 104 1774 (1982); 109 5437 (1987) JOC 50 2607 (1985) CL 85 (1986)
NaMnO ₄ ·H ₂ O	TL 22 1655 (1981)
KMnO ₄	JCS 633 (1939); 2685 (1950) BCSJ 36 1264 (1963) TL 28 5263 (1987)
KMnO ₄ (phase transfer)	TL 1511 (1974) JACS 109 7280 (1987)
KMnO ₄ , H ₂ SO ₄	TL 32 1059 (1991)
(<i>n</i> -Bu ₄ N)MnO ₄ , py (R = aryl)	CC 253 (1978)
Cu(MnO ₄) ₂ ·8H ₂ O	JOC 47 2790 (1982)
Zn(MnO ₄) ₂ ·6H ₂ O	J Biol Chem 241 3970 (1966) JOC 50 5480 (1985)
cat RuO ₂ ·2H ₂ O, electrolysis	JOC 51 155 (1986)
RuO ₄	JACS 80 6682 (1958)
cat K ₂ Ru ₂ O ₄ , K ₂ SO ₅	CC 58 (1979)
RuCl ₃ , K ₂ S ₂ O ₈	TL 28 4965 (1987)
cat RuCl ₃ , K ₂ S ₂ O ₈ , KOH	TL 33 7719 (1992)
AgO	TL 5685 (1968)
NaOCl, cat TEMPO, NaHCO ₃ , KBr, <i>n</i> -Bu ₄ NCl	TL 34 1181 (1993)
NaOCl, cat TEMPO, KBr, Aliquat 336, NaHCO ₃	JOC 58 3589 (1993)
NaOCl, cat 4-MeO-TEMPO, KBr, Aliquat 336	JOC 52 2559 (1987)
NaBrO ₂ ·3H ₂ O, cat 4-PhCO ₂ -TEMPO, NaHCO ₃	JOC 55 462 (1990)
NaIO ₄ , cat RuCl ₃ ·H ₂ O, H ₂ O, CH ₃ CN, CCl ₄	JOC 46 3936 (1981); 50 5696 (1985); 55 6051 (1990); 57 4142 (1992); 58 4758 (1993) TL 31 5023 (1990) JACS 113 8045 (1991)

NaIO_4 , cat RuO_2 , H_2O

TL 28 6425 (1987)

JOC 53 3046 (1988); 55 3772 (1990)

H_5IO_6 , cat $\text{RuCl}_3 \cdot \text{H}_2\text{O}$, H_2O , CH_3CN , CCl_4

JOC 50 1560 (1985); 55 1928 (1990)

electrolysis [$\text{Ni}(\text{OH})_2$ anode]

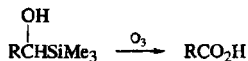
Syn 513 (1979)

Tetr 38 3299 (1982)

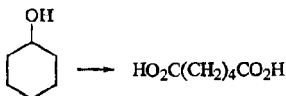
Pseudomonas aeruginosa (R = allenyl,
enantioselective)

TL 21 1711 (1980)

Appl Microbiol Biotechnol 21 258 (1985)



TL 33 6767 (1992)



HNO_3

Rec Trav Chim 24 19 (1905)

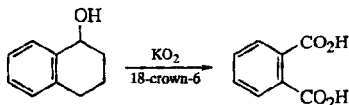
JACS 52 3235 (1930)

Org Syn Coll Vol 1 18 (1941)

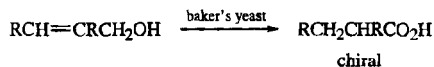
KMnO_4

Ber 41 575 (1908), 55B 3526 (1922)

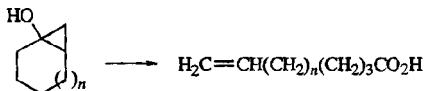
J Chem Ed 10 113 (1933)



JOC 55 2159 (1990)



TL 29 2197 (1988)



Reagent

n

$\text{Pb}(\text{OAc})_4$

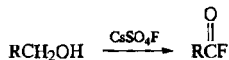
1

TL 4013 (1977)

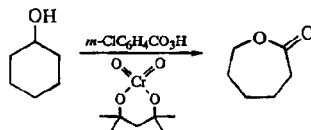
$\text{PhI}(\text{OAc})_2$

1-3

TL 36 6907 (1995)



TL 30 6095 (1989)



TL 33 5699 (1992)

 $\text{Ca}(\text{OCl})_2$

TL 23 35 (1982)

 $\text{NaBrO}_2 \cdot 3\text{H}_2\text{O}$, cat 4- PhCO_2 -TEMPO, HOAc

JOC 55 462 (1990)

KI, H_2O , electrolysis

TL 165 (1979)

 $\text{Na}_2\text{Cr}_2\text{O}_7$, H_2SO_4

Org Syn Coll Vol 1 138 (1941)

 $t\text{-BuO}_2\text{H}$, cat $(\text{PhCH}_2\text{NMe}_3)\text{OMoBr}_4$

TL 25 4417 (1984)

cat $\text{H}_2\text{Ru}(\text{PPh}_3)_4$

TL 22 5327 (1981)

JOC 52 4319 (1987)

cat $\text{Ru}_3(\text{CO})_{12}$, $\text{PhC}\equiv\text{CPh}$

TL 22 1541 (1981)

cat PdCl_2 , K_2CO_3 , CCl_4

CL 1171 (1981)

cat $\text{Pd}(\text{OAc})_2$, cat PPh_3 , ArBr , K_2CO_3

JOC 48 1286 (1983)

 $(\text{COCl})_2$ -DMSO, $\text{Et}_3\text{N}/(\text{CH}_3)_2\text{C}(\text{OH})\text{CN}$, $\text{Et}_3\text{N}/(\text{COCl})_2$ -DMSO, $\text{Et}_3\text{N}/\text{MeOH}$ ($\text{R}' = \text{Me}$)

JOC 51 3023 (1986)

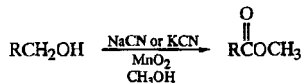
 $\text{Ca}(\text{OCl})_2$, HOAc, CH_3CN , MeOH ($\text{R}' = \text{Me}$)

TL 34 2741 (1993)

 $\text{CrO}_3 \cdot 2\text{py}$, Ac_2O , $t\text{-BuOH}$ ($\text{R}' = t\text{-Bu}$)

JOC 49 4735 (1984)

TL 27 3049 (1986)

 R

aryl

TL 28 5157 (1987)

vinylic

JACS 90 5616 (1968); 114 2567 (1992)

JOC 51 253 (1986)

 MsCl , $\text{Et}_3\text{N}/\text{CsO}_2\text{CEt}$ ($\text{R}' = \text{Et}$)

JOC 46 4321 (1981)

 $\text{Zn}(\text{O}_2\text{CR}')_2$ ($\text{R}' = \text{Me}$, Ph), PPh_3 ,

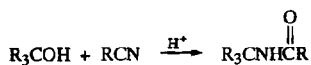
Syn Commun 16 611 (1986)

 $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$

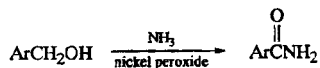
See also page 1932, Section 3; page 1951, Section 8; page 1955, Section 14; and page 1969, Section 20.



See page 1641, Section 11.

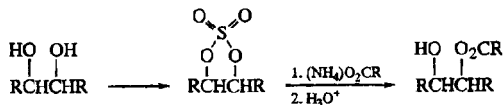


See page 1988, Section 33.



CC 17 (1966)

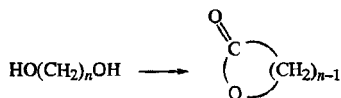
14. Diols

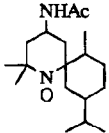
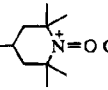


See page 1932, Section 3.

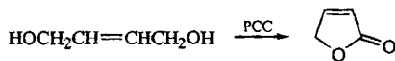
H₂O₂, cat Na₂WO₄·2H₂O·H₃PO₄ IOC 51 1599 (1986)H₂O₂, cat [C₃H₅N(CH₂)₁₅CH₃]₃PW₁₂O₄₀ IOC 53 3587 (1988)*t*-BuO₂H, cat VO(acac)₂ TL 24 5009 (1983)*t*-BuO₂H, cat Mo(CO)₆, cat [C₃H₅N(CH₂)₁₅CH₃]₃Cl, MgSO₄ Syn 59 (1986)NaOCl, cat RuCl₃·3H₂O CC 1420 (1970)H₅IO₆, cat RuCl₃·H₂O IOC 55 1928 (1990)NaIO₄, cat RuCl₃·H₂O IOC 46 3936 (1981)

TL 34 7781 (1993)

NaIO₄/AgNO₃, KOH JACS 107 3285 (1985)cat RuO₂·2H₂O, electrolysis IOC 51 155 (1986)KMnO₄ IOC 50 3007 (1985)Review: Heterocycles 14 661 (1980) (*n* = 4)

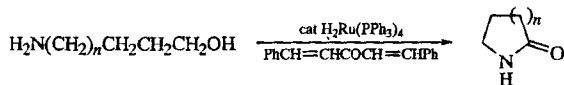
horse liver alcohol dehydrogenase ($n = 4, 5$; chiral)	CC 469 (1977); 515 (1980) JACS 104 4659 (1982); 106 1461 (1984); 107 2521 (1985) Can J Chem 60 2007 (1982) Org Syn 63 10 (1984) Org Syn Coll Vol 7 406 (1990)
O ₂ , cat Pt ($n = 4$)	TL 3899 (1973); 4045 (1976) JACS 98 3379 (1976); 102 3964 (1980) JOC 58 1030 (1993)
H ₂ O ₂ , [C ₃ H ₅ N(CH ₂) ₁₅ CH ₃] ₃ PMo ₁₂ O ₄₀ ($n = 4-6$)	JOC 52 1868 (1987)
H ₂ O ₂ , [C ₃ H ₅ N(CH ₂) ₁₅ CH ₃] ₃ PW ₁₂ O ₄₀ ($n = 4-7, 11, 13$)	JOC 53 5549 (1988)
m -ClC ₆ H ₄ CO ₃ H, cat  ($n = 4$)	JOC 58 4837 (1993)
trichloromelamine ($n = 4$)	JOC 58 5003 (1993)
MeO-  Cl ⁻ ($n = 4, 5$)	JOC 50 3930 (1985)
LiOCl, cat 4-MeO-TEMPO, NaHCO ₃ ($n = 4$)	JOC 54 2970 (1989)
LiOCl, cat TEMPO, NaHCO ₃ ($n = 5$)	JOC 54 2970 (1989)
NaOCl, cat TEMPO ($n = 5$)	JOC 54 2970 (1989)
NaBr, cat 4-PhCO ₂ -TEMPO, electrolysis ($n = 4, 5$)	JOC 56 2416 (1991)
NaBrO ₂ , cat 4-PhCO ₂ -TEMPO, NaHCO ₃ ($n = 4, 5$)	JOC 55 462 (1990) TL 34 5597 (1993)
NaBrO ₃ ($n = 4-6$)	CL 1097 (1983)
NIS, AgOAc ($n = 4, 5$)	JOC 52 5472 (1987)
CrO ₃ , py ($n = 4, 6$)	JACS 76 527 (1954) JOC 28 323 (1963) TL 27 1445 (1986)
Na ₂ Cr ₂ O ₇ , H ₂ SO ₄ ($n = 4, 5$)	JOC 28 323 (1963); 45 1828 (1980)
MnO ₂ ($n = 4, 5$; allylic to 2-alkylidene-4 or 5-alkanolide)	JACS 98 4312 (1976) TL 111 (1978) Syn Commun 13 237 (1983)
BaMnO ₄ ($n = 4$)	JCS Perkin I 1579 (1983) JOC 52 325 (1987)
KMnO ₄ ($n = 4$)	JOC 28 323 (1963); 42 1623 (1977)
NMO, cat (n -Pr ₄ N)RuO ₄ , molecular sieves ($n = 4, 5$)	SL 829 (1991) JOC 60 4813 (1995)

NMO, cat $\text{RuCl}_2(\text{PPh}_3)_3$ ($n = 5$)	TL 23 807 (1982) JOC 58 2923 (1993)
NMO, cat $\text{RuCl}_2(\text{PPh}_3)_3 / \text{Ag}_2\text{CO}_3$, Celite ($n = 5$)	TL 27 3311 (1986)
cat $\text{Ru}_3(\text{CO})_{12}$, $\text{PhC}\equiv\text{CPh}$ ($n = 4, 5$)	JOMC 226 C1 (1982)
cat $\text{RuO}_2 \cdot 2\text{H}_2\text{O}$, electrolysis ($n = 4, 5$)	JOC 51 155 (1986)
cat RuCl_2L_3 or $\text{Ru}_2\text{Cl}_4\text{L}_3$, $\text{PhCH}=\text{CHCOCH}_3$, Et_3N ($n = 4, 5$)	TL 24 2677 (1983)
cat $\text{H}_2\text{Ru}(\text{PPh}_3)_4$, $\text{PhCH}=\text{CHCOPh}$ ($n = 5$)	J Mol Catal 7 337 (1980)
cat $\text{H}_2\text{Ru}(\text{PPh}_3)_4$, $\text{PhCH}=\text{CHCOCH}_3$ ($n = 4, 5$)	TL 27 365 (1986) JOC 51 2034 (1986)
cat $\text{H}_2\text{Ru}(\text{PPh}_3)_4$, CH_3COCH_3 ($n = 4, 5$)	TL 22 5327 (1981); 32 5383 (1991); 33 3935 (1992) JOC 52 4319 (1987)
cat $\text{HRh}(\text{PPh}_3)_4$, $\text{CH}_3\text{COCH}=\text{CHPh}$ ($n = 4, 5$)	JOC 51 2822 (1986)
Raney Ni ($n = 4$)	JOC 21 1325 (1956)
$\text{Ni}(\text{O}_2\text{CR})_2$, Br_2 ($n = 4$)	Syn Commun 10 881 (1980) JOC 46 4806 (1981); 48 476 (1983)
cat $\text{Pd}(\text{OAc})_2$, cat PPh_3 , ArBr , K_2CO_3 ($n = 4$)	JOC 48 1286 (1983)
copper chromite ($n = 4, 5$)	JACS 68 1385 (1946); 69 1545 (1947)
AgCO_3 , Celite ($n = 4-6$)	Tetr 31 171, 987 (1975) TL 4045 (1976); 22 3721, 3725 (1981); 31 4305 (1990) JOC 43 1086 (1978); 50 3017 (1985); 52 325 (1987); 57 2575 (1992) JACS 104 5523 (1982); 117 10239 (1995) JCS Perkin I 1579 (1983)



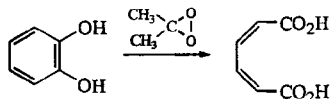
JOC 54 1491 (1989)

15. Aminoalcohols



SL 693 (1991)

16. Phenols



TL 32 5445 (1991)

17. Aldehydes and Derivatives

Pb(OAc)₄

JACS 79 1938 (1957)

Compt Rend 250 4174 (1960)

Pb(OAc)₄, BF₃

BSCF 4083 (1968)



air

JOC 51 449 (1986)

O₂, cat NPV₆Mo₆

JOC 58 6421 (1993)

O₂, cat Mn(II) stearate

JOC 52 287 (1987)

O₂, cat Fe[2-(acetooacetoxy)ethyl methacrylate]₃

TL 35 4193 (1994)

O₂, cat CoCl₂, Ac₂O (R = aryl, vinylic > alkyl)

TL 33 7961 (1992)

JOC 58 5518 (1993)

O₂, cat CoCl₂, Ac₂O, *n*-C₃H₇CHO (R = aryl)

TL 35 2959 (1994)

O₂, cat Pt

JOC 57 6861 (1992)

H₂O₂

"Hydrogen Peroxide in Organic Chemistry," DuPont (1962), p 56

H₂O₂, K₂CO₃, MeOH

Syn 1024 (1986)

H₂O₂, cat PhSeO₂H

TL 29 1967 (1988)

H₂O₂, (NH₄)₆Mo₇O₂₄·4H₂O, CeCl₃·7H₂O,
n-Bu₄NCl, K₂CO₃

TL 25 173 (1984)

H₂O₂, cat [(*n*-C₈H₁₇)₃NCH₃]₃PO₄[W(O)(O₂)₂]₄

JOC 56 5924 (1991)

t-BuO₂H, cat (PhCH₂NMe₃)OMoBr₄

TL 25 4417 (1984)

nickel peroxide, NaOH (R = aryl)

Chem Pharm Bull 26 299 (1978)

NaBO₃·4H₂O, HOAc (R = aryl)

Tetr 45 3299 (1989)

CF₃C(OH)(O₂H)CF₃

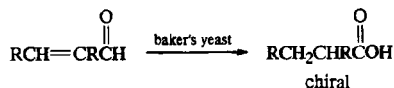
TL 21 685 (1980)



TL 30 5567 (1989)

PhCO ₃ H	JOC 34 3985 (1969)
<i>m</i> -ClC ₆ H ₄ CO ₃ H	JOC 55 5528 (1990)
magnesium monoperoxyphthalate	TL 36 837 (1995)
Oxone [®] (K ₂ SO ₄ ·2KHSO ₅ ·KHSO ₄)	TL 36 833 (1995)
NaHSO ₃ / Ac ₂ O, DMSO / H ₂ O	TL 27 3995 (1986)
HNO ₃	Org Syn Coll Vol I 166 (1941)
$\left[\text{ClCH}_2\text{N}^+\text{C}_6\text{H}_4\text{N}^+\text{F} \right] (\text{BF}_4)_2$ (R = aryl)	SL 831 (1994)
NaClO ₂ , H ₂ O, CH ₃ CN	Org Prep Proc Int 26 123 (1994)
NaClO ₂ , CH ₃ CH=C(CH ₃) ₂	JOC 45 1175 (1980)
NaClO ₂ , (K)NaH ₂ PO ₄ , CH ₃ CH=C(CH ₃) ₂	Tetr 37 2091 (1981) JOC 50 470 (1985); 60 3626 (1995) JACS 109 6719 (1987); 110 5806 (1988); 111 3728, 5761 (1989); 112 775 (1990) TL 28 5759, 5763 (1987); 36 7693 (1995)
NaClO ₂ , NaH ₂ PO ₄ , (CH ₃) ₂ C=CH ₂	JACS 106 7217 (1984) TL 27 3533 (1986)
NaClO ₂ , H ₂ O ₂ , NaH ₂ PO ₄	JOC 51 567 (1986); 59 4749, 6703 (1994)
NaClO ₂ , H ₂ NSO ₂ OH	Acta Chem Scand 27 888 (1973) JOC 51 3007 (1986); 59 406, 6703 (1994)
NaClO ₂ , HOAc	Methods Carbohydr Chem 3 182 (1963)
NaClO ₂ , resorcinol, acetate buffer	Acta Chem Scand 27 888 (1973)
Ca(OCl) ₂	TL 23 3131 (1982)
NBS, H ₂ O	JACS 78 1689 (1956)
I ₂ , KOH, H ₂ O	TL 33 4329 (1992)
CrO ₃ , Ac ₂ O	JACS 86 2612 (1964)
CrO ₃ , H ₂ SO ₄	JACS 113 7388 (1991)
K ₂ Cr ₂ O ₇ , H ₂ SO ₄	JACS 80 3022, 3030 (1958); 107 199, 4980 (1985); 108 1039 (1986); 112 6690 (1990)
pyridinium fluorochromate	JOC 56 5111 (1991)
(C ₃ H ₅ NH) ₂ Cr ₂ O ₇ (PDC)	TL 399 (1979) JOC 50 2095 (1985)
(bipy) ₂ H ₂ CrOCl ₅	Syn Commun 10 951 (1980)
(phen) ₂ H ₂ CrOCl ₅	Syn Commun 10 951 (1980)
(bipy)CrOCl ₅	Syn Commun 10 951 (1980)
NaMnO ₄ ·H ₂ O	TL 22 1655 (1981)
KMnO ₄	Org Syn Coll Vol 2 315, 538 (1943) JACS 106 3297 (1984); 107 199 (1985); 114 9309 (1992)

KMnO ₄ , 18-crown-6	JACS 94 4024 (1972) TL 27 4537 (1986)
KMnO ₄ , MgSO ₄	JACS 109 7122 (1987)
KMnO ₄ , <i>t</i> -BuOH, 5% (K)NaH ₂ PO ₄	TL 27 4537 (1986) JACS 109 7575 (1987); 114 10181 (1992)
(<i>n</i> -Bu ₄ N)MnO ₄ , py	CC 253 (1978) JOC 53 5903 (1988)
(PhCH ₂ NEt ₃)MnO ₄ , CH ₂ Cl ₂ , HOAc	Monatsh 110 1471 (1979)
Cu(MnO ₄) ₂ ·8H ₂ O	JOC 47 2790 (1982)
RuO ₄	JACS 80 6682 (1958)
cat RuO ₂ ·2H ₂ O, electrolysis	JOC 51 155 (1986)
cat RuO ₂ , NaIO ₄	JOC 52 622 (1987)
cat RuCl ₂ (PPh ₃) ₄ , PhIO	TL 22 2361 (1981)
cat RuCl ₃ ·H ₂ O, NaIO ₄ , CCl ₄ , CH ₃ CN, H ₂ O	JOC 46 3936 (1981)
cat H ₂ Ru(PPh ₃) ₄ , PhCH=CHCOCH ₃ , H ₂ O	JOC 52 4319 (1987)
Ag ₂ O	JACS 73 2590 (1951); 92 336 (1970); 106 1029 (1984); 107 7978 (1985); 112 6942 (1990) Org Syn Coll Vol 4 919 (1963) Tetr 24 6583 (1968) JOC 44 1022 (1979); 50 2981 (1985); 51 956 (1986); 54 2183 (1989) Syn 74 (1981) JCS Perkin I 461 (1982) TL 36 5861 (1995)
AgO	TL 5685 (1968)
AgO, NaCN	JACS 90 5616 (1968)
AgNO ₃ , NaOH, H ₂ O ₂ , H ₂ O, O ₂	Ber 93 2743 (1960)



TL 29 2197 (1988)



X

Reagent(s)

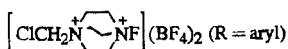
F

CsSO₄F

TL 30 6095 (1989)

JOC 57 5334 (1992)

SL 831 (1994)



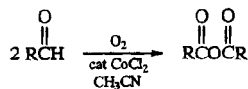
Cl

Cl₂

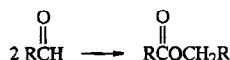
Org Syn Coll Vol 1 155 (1941)



<u>X</u>	<u>Reagent(s)</u>	
	(PhCO ₂) ₂ , CCl ₄	JACS 69 2916 (1947)
Br	NBS, hv	TL 3809 (1979)
	NBS, AIBN	TL 31 7237 (1990)



JOC 58 5518 (1993)

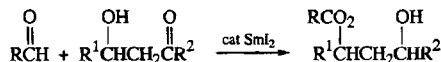


RCH ₂ ONa	Org Syn Coll Vol 1 104 (1941)
B(OH) ₃	JOC 38 1433 (1973)
Al(OR) ₃	Chem Zentr 77 1309, 1554, 1556 (1906)
	Org Syn Coll Vol 1 104 (1941)
	JACS 69 2605 (1947); 74 5133 (1952)
	JOC 33 3310 (1968)
Fe ₂ (CO) ₉	JOC 54 2003 (1989)
cat H ₂ Ru(PPh ₃) ₄ , H ₂ O	JOC 52 4319 (1987)
cat Ru ₃ (CO) ₁₂ , H ₂ O, PhC≡CPh	TL 22 1541 (1981)

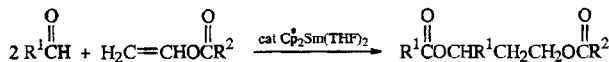


O ₂ , cat HCl, hv, R'OH (R = aryl)	CL 475 (1974)
O ₃ , KOH, R'OH	TL 1627 (1978)
<i>t</i> -BuO ₂ H, cat (PhCH ₂ NMe ₃)OMoBr ₄ , R'OH	TL 25 4417 (1984)
PhNO ₂ , KCN, R'OH, phase transfer catalyst (R = aryl)	Tetr 38 337 (1982)
NaHSO ₃ /Ac ₂ O, DMSO/R'OH	TL 27 3995 (1986)
H ₂ SO ₅ , R'OH	JOC 33 2525 (1968)
(NH ₄) ₂ S ₂ O ₈ , H ₂ SO ₄ , MeOH	Tetr 37 2091 (1981)
$\left[\text{ClCH}_2\text{N}^+(\text{CH}_2)_3\text{NF} \right] (\text{BF}_4)_2 / \text{R}'\text{OH}$ (R = aryl)	SL 831 (1994)
HOCl, R'OH	TL 23 4647 (1982)
NaOCl, HOAc, MeOH	TL 23 4647 (1982)
Ca(OCl) ₂ , HOAc, CH ₃ CN, R'OH, molecular sieves	TL 34 2741 (1993)

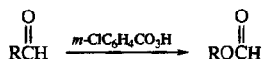
<i>t</i> -BuOCl/R'OH, Et ₃ N or py	JOC 47 1360 (1982)
Br ₂ , R'OH, NaHCO ₃ , H ₂ O	TL 29 5087 (1988) JACS 117 5757 (1995)
Br ₂ , R'OH, NaHCO ₃ , HMPA	TL 31 2273 (1990)
NBS, hν/R'OH	TL 3809 (1979)
NBS, R'OSiMe ₃	JOC 43 371 (1978) SL 347 (1990)
NBS, R'OSn(<i>n</i> -Bu) ₃	JACS 98 1629 (1976)
I ₂ , CH ₃ OH, KOH	JCS C 1693 (1968) JOC 50 2707 (1985) TL 33 4329 (1992); 34 7903 (1993)
NIS, K ₂ CO ₃ , R'OH	JOC 54 1213 (1989)
PDC, CH ₃ OH	TL 28 3235 (1987) JOC 60 2200 (1995)
MnO ₂ , NaCN or KCN, CH ₃ OH (R = vinylic, aryl)	JACS 90 5616 (1968); 113 5402 (1991) Ber 103 3774 (1970) JOC 51 253, 3070 (1986) TL 36 2397, 5797 (1995)
Me ₃ SiCl, cat ZnI ₂ /H ₃ O ⁺ /MnO ₂ , MeOH	Tetr 37 2091 (1981)
cat Ru ₃ (CO) ₁₂ , RCH ₂ OH (R' = R), PhC≡CPh	TL 22 1541 (1981)
cat H ₂ Ru(PPh ₃) ₄ , R'OH	JOC 52 4319 (1987)
electrolysis, R'OH	JOC 50 4967 (1985)
electrolysis, CH ₃ OH, cat KI	JOC 53 218 (1988)
electrolysis, NaCN, MeOH	BCSJ 55 335 (1982)
electrolysis, cat flavin, cat thiazolium ion, NEt ₃ , Et ₄ NBr, MeOH (R = aryl)	JACS 114 1503 (1992)



JACS 112 6447 (1990); 115 7906 (1993)



JOC 60 4974 (1995)

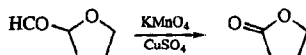


TL 36 3401 (1995)



Review: Org Rxs 43 251 (1993)

O_2 , Me_2CHCHO , cat $\text{M}(\text{acac})_2$ ($\text{M} = \text{Ni}, \text{Cu}$)	TL 36 6679 (1995)
H_2O_2 , SeO_2	TL 27 6299 (1986)
PhCO_3H	JOC 34 3985 (1969)
$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$	JCS Perkin I 1353 (1974)
$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$, KF	TL 22 3895 (1981)
$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$, Na_2HPO_4	JOC 53 1584 (1988)



TL 34 1979 (1993)

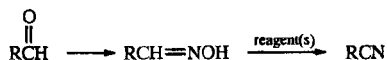


NH_3 , nickel peroxide ($\text{R} = \text{aryl, vinylic}$)	CC 17 (1966)
R_2NH , NaCN , MnO_2 ($\text{R} = \text{aryl, vinylic}$)	CC 733 (1971)
R_2NH , KCN , HCl/O_2 , $\text{KO}-t\text{-Bu}$	SL 733 (1990)
R_2NH , cat $\text{H}_2\text{Ru}(\text{PPh}_3)_4$	SL 693 (1991)
$\left[\text{ClCH}_2\text{N}^+\text{C}_6\text{H}_4\text{N}^+\text{F}\right](\text{BF}_4)_2/\text{R}_2\text{NH}(\text{ArCHO})$	SL 831 (1994)
NBS , $h\nu/\text{RNH}_2$	TL 3809 (1979)
NBS , $\text{AIBN}/\text{R}_2\text{NH}$	TL 31 7237 (1990); 34 8213 (1993)
$\text{Me}_3\text{SiN}_3/\Delta/\text{MeOH}$ ($\text{R} = \text{H}$)	Ann 266 (1975)
$\text{Me}_3\text{SiCN}/\text{LDA}/\text{Ph}_2\text{P}(\text{O})\text{ONMe}_2/\text{H}_3\text{O}^+$	TL 23 3255 (1982)
$\text{NaHSO}_3/\text{Ac}_2\text{O}$, DMSO/HNR_2	TL 27 3995 (1986)





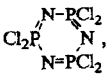
NH_3 , electrolysis, cat NaOMe , cat KI , MeOH	JOC 53 218 (1988)
NH_3 , O_2 , cat CuCl_2 , NaOMe , MeOH	Rec Trav Chim 82 757 (1963)
NH_3 , I_2 , NaOMe , MeOH	BCSJ 39 854 (1966)
NH_3 , $\text{Pb}(\text{OAc})_4$	Chem Ind 988 (1965)
$\text{HONH}_2\cdot\text{HCl}$, MgSO_4 , $p\text{-TsOH}$	Syn Commun 13 219 (1983)
$\text{HONH}_2\cdot\text{HCl}/\text{py}/\text{SeO}_2$	Syn 722 (1979)
$\text{HONH}_2\cdot\text{HCl}/\text{Ac}_2\text{O}$	JOC 58 4642 (1993)
$\text{HONH}_2\cdot\text{HCl}$, $\text{NaOH}/\text{cat NaCN}$, cat Aliquot 336	CL 1295 (1977)






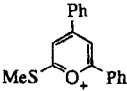
HONH ₂ ·HCl, py / CuSO ₄ ·5H ₂ O / Et ₃ N / DCC	Ber 107 1221 (1974) JOC 59 7876 (1994)
H ₂ NOSO ₃ H / py	JOC 59 3512 (1994)
2,4-(NO ₂) ₂ C ₆ H ₃ ONH ₂ / KOH or Et ₃ N	JOC 40 126 (1975)
CF ₃ CO ₂ NHCOCF ₃ , py	JACS 81 6340 (1959)
NaN ₃ , SiCl ₄	TL 36 2639 (1995)

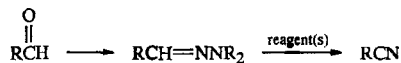


Review: Chem Rev 42 189 (1948)

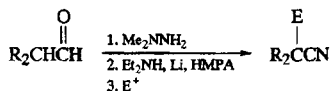
Reagent(s)

HCCl ₃ , NaOH, cat (PhCH ₂ NEt ₃)Cl	TL 2121 (1973)
Cl ₃ CCOCl	Syn 1037 (1986)
Cl ₃ CCOCl, Et ₃ N	Syn 748 (1983)
PhOCOCl, py	Can J Chem 49 1321 (1971)
(CH ₃ CO) ₂ O	JOC 56 1334 (1991)
(CF ₃ CO) ₂ O, py	Syn 56 (1979)
CF ₃ CON ₂	BCSJ 54 1579 (1981)
() ₂ CO	CC 628 (1973)
Cl ₃ CCN	JOC 38 2241 (1973)
 , Cl, py	CC 1226 (1972)
(Me ₂ N=CHCl)Cl	TL 22 1599 (1981)
(Me ₂ N=CCl ₂)Cl	Syn 563 (1974)
(MeC≡NEt)BF ₄	Syn 401 (1975)
cat KCN, cat 18-crown-6	CL 1295 (1977)
CCl ₄ , Ph ₂ P-polymer	Syn 41 (1977)
 , Et ₃ N	JOC 38 1060 (1973)
(EtO) ₃ PI ₂ , Et ₃ N	TL 1725 (1979)
PI ₃ , Et ₃ N	CC 544 (1980)
P ₂ I ₄ , py ?	Syn 905 (1978)
POCl ₃ , Et ₃ N	Z Naturforsch B 33 1033 (1978)

PhOP(O)Cl ₂	Z Naturforsch B 33 1033 (1978)
4-Cl ₂ P(O)-TEMPO	Z Naturforsch B 33 1033 (1978)
(PhO) ₂ POCl	Z Naturforsch B 33 1033 (1978)
4-PhOP(O)Cl-TEMPO	Z Naturforsch B 33 1033 (1978)
(PhO) ₂ P(O)N 	Z Naturforsch B 33 1033 (1978)
(PhO)P(O)() ₂	Z Naturforsch B 33 1033 (1978)
OP() ₃	Z Naturforsch B 33 1033 (1978)
PhP(O)(OR)N  (R = 4-TEMPO)	Z Naturforsch B 33 1033 (1978)
ROP(O)() ₂ (R = 4-TEMPO)	Z Naturforsch B 33 1033 (1978)
(PhO) ₂ P(O)H, Et ₃ N	JOC 34 2805 (1969)
SCl ₂ , Et ₃ N (R = aryl)	Z Naturforsch B 34 511 (1979)
S ₂ Cl ₂ , Et ₃ N (R = aryl)	Z Naturforsch B 34 511 (1979)
Cl ₃ CSCl, Et ₃ N (R = aryl)	Z Naturforsch B 34 511 (1979)
PhSCl, Et ₃ N	Z Naturforsch B 34 511 (1979)
p-ClC ₆ H ₄ OC(S)Cl	CC 1014 (1970)
Me ₂ SCl ₂ , Et ₃ N	Syn Commun 5 423 (1975)
PhOSOCI, py	Syn 502 (1975)
FSO ₂ Cl, Et ₃ N	Syn 659 (1980)
SOCl ₂ , DMF, py	TL 25 3365 (1984)
ClSO ₂ NCO, Et ₃ N	Syn 227 (1979)
(CF ₃ SO ₂) ₂ O, Et ₃ N	TL 603 (1976)
Me ₃ N·SO ₃ , Et ₃ N	Syn 702 (1978)
 BF ₄ ⁻ , Et ₃ N	Syn 1016 (1982)
CS ₂ , (n-Bu ₄ N)HSO ₄ , NaOH	CL 929 (1983) JOC 59 7125 (1994)
PhSeCl, Et ₃ N	Z Naturforsch B 34 511 (1979)
PhSe(O)Cl, Et ₃ N	Z Naturforsch B 34 511 (1979)
SeO ₂ or cat SeO ₂	Syn 703 (1978)
TiCl ₄ , py	TL 559 (1971)
cat CuOAc·H ₂ O	Syn 741 (1983)
NaX (X = Cl, Br, I) or Et ₄ NOTs, electrolysis	JOC 54 2249 (1989)


Reagent(s)

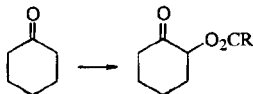
H_2O_2	JOC 31 4100 (1966) (R = aryl, vinylic) J Prakt Chem 336 467 (1994)
H_2O_2 , cat SeO_2 (R = aryl, vinylic)	Syn 223 (1989)
H_2O_2 , cat 2-nitrobenzeneseleninic acid (R = aryl, vinylic)	Syn 223 (1989)
$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$	Syn 223 (1989) J Prakt Chem 336 467 (1994)
$o\text{-HO}_2\text{CC}_6\text{H}_4\text{CO}_3\text{H}\cdot 6\text{H}_2\text{O}$	SL 1054 (1994)
magnesium monoperoxyphthalate hexahydrate	TL 34 141 (1993) SL 869 (1995)
MeI/DBU	JOC 55 3374 (1990)
MeI or MeOTs/NaOMe	JOC 27 4372 (1962); 55 6177 (1990)
LiNEt_2	Syn 237 (1976)
cat CuCl_2	Ber 43 2297 (1910)



Syn 238 (1976)

18. Ketones

See also page 1843, Section 7.



$\text{Pb}(\text{OAc})_4$	JCS 4426 (1955) Austral J Chem 13 121 (1960) Syn 567 (1973) (review) JACS 107 5576 (1985) TL 36 1027 (1995)
$\text{Pb}(\text{OAc})_4$, $h\nu$	JCS C 2484 (1969)
$\text{Pb}(\text{OAc})_4$, cat $\text{BF}_3\cdot\text{OEt}_2$	JCS 4472 (1961) Syn 567 (1973) (review); 898 (1979) TL 32 4577 (1991)
$\text{Mn}(\text{OAc})_3$	JOC 53 4945 (1988); 55 504 (1990); 58 4952 (1993)

Mn(OAc)₃, RCO₂H or Mn(O₂CR)₃

JOC 54 4020 (1989)

Hg(OAc)₂

Naturwiss 35 125 (1948)

Ann 561 165 (1949); 581 59 (1953)

Helv 35 1615 (1952)

JCS 3512 (1953); 705 (1954)

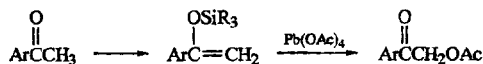
JACS 79 4465 (1957)

Ber 93 1374 (1960)

JOC 28 1705 (1963)

Syn 567 (1973) (review)

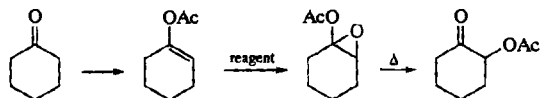
R. C. Larock, "Organomercury Compounds in Organic Synthesis," Springer, New York (1985), p 205 (review)



Syn Commun 6 59 (1976)

M = ArTiO₂CCF₃, ArPb(OAc)₂, Hg (as R₂Hg)

JOC 53 1022 (1988)

Reagent

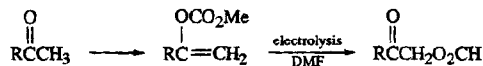
JOC 57 6379 (1992); 59 6828 (1994)

PhCO₂H

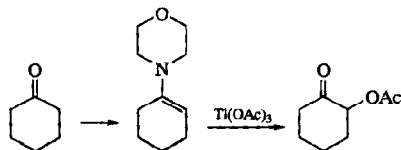
JOC 26 4563 (1961)

m-ClC₆H₄CO₂H

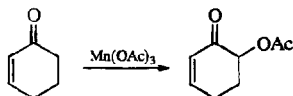
JOC 59 6395 (1994)



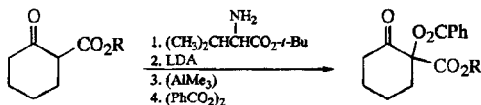
JOC 60 5658 (1995)



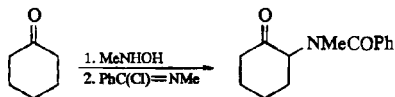
JOC 33 3359 (1968)



TL 25 5839 (1984), 30 5989 (1989)



TL 32 5899 (1991)



TL 35 5977 (1994)

NaNO₂, py·(HF)_x (R = 3° alkyl, aryl)

SL 41 (1991)

HNO₃/KMnO₄ (R = aryl)

Org Syn Coll Vol 3 791 (1955)

NaOCl (R = aryl)

Org Syn Coll Vol 2 428 (1943)

KOCi (R = vinylic)

Org Syn Coll Vol 3 302 (1955)

Br₂, NaOH/HCl (R = 1°, 2° alkyl)

Org Syn Coll Vol 5 8 (1973)

JACS 107 2033 (1985)

JOC 58 1900 (1993)

I₂, KI, NaOH (R = 1° alkyl)

JACS 113 1791 (1991)

I₂, py/NaOH (R = aryl)

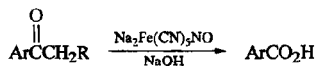
JACS 66 894 (1944)

C₆F₅I(O₂CCF₃)₂, H₂O, C₆H₆ (R = aryl)

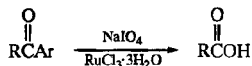
CC 202 (1987)

Na₂Cr₂O₇, HOAc (R = aryl)

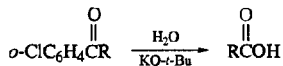
Org Syn Coll Vol 3 420 (1955)



SL 165 (1992)



JOC 55 157 (1990)



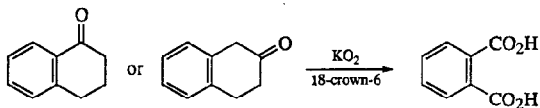
JCS 1408 (1948)

JCS C 455 (1971)

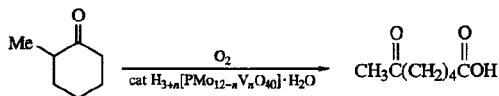
TL 3825 (1971)

Syn 360 (1973)

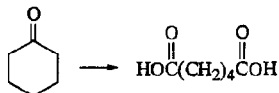
Org Syn Coll Vol 6 625 (1988)



JOC 55 2159 (1990)



JOC 58 5663 (1993)

 O_2 , cat $\text{H}_7[\text{PMo}_8\text{V}_4\text{O}_{40}] \cdot 12\text{H}_2\text{O}$

JOC 58 5663 (1993)

 KO_2 (phase transfer)

TL 3689 (1978)

 HNO_3

Rec Trav Chim 24 19 (1905)

 $\text{C}_6\text{H}_5\text{I}(\text{O}_2\text{CCF}_3)_2$, H_2O , C_6H_6

CC 202 (1987)

 KMnO_4

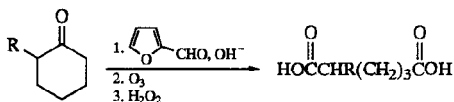
Ber 39 2202 (1906)

 $\text{Zn}(\text{MnO}_4)_2$, silica gel

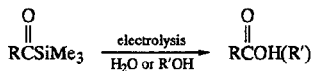
JACS 105 7755 (1983)

cat $\text{Re}_2(\text{CO})_{10}$, KOH , K_2CO_3 , cat PEG-400

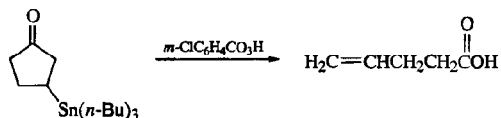
JOC 53 808 (1988)



TL 34 7789 (1993)



JOC 57 4877 (1992)



JACS 112 6729 (1990)



Reviews:

Chem Rev 45 385 (1949)

Org Rxs 9 73 (1957); 43 251 (1993)

P. A. S. Smith, "Molecular Rearrangements," Ed. P. de Mayo, Interscience, New York (1963), Vol 1, pp 577-589

Quart Rev 21 429 (1967)

B. Plesnicar, "Oxidation in Organic Chemistry," Ed. W. S. Trahanovsky, Academic Press, New York (1978), pp 254-262

Tetr 37 2697 (1981)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 5.1, p 671

Topics Curr Chem 164 1 (1993)

O ₂ , PhCHO	JOC 59 2915 (1994)
O ₂ , PhCHO, cat NPV ₆ Mo ₆	JOC 58 6421 (1993)
O ₂ , PhCHO, cat MnO ₂	SL 1037 (1994)
O ₂ , RCHO, cat Fe ₂ O ₃	TL 33 7557 (1992)
O ₂ , Me ₂ CHCHO, cat Fe[2-(acetoacetoxy)ethyl methacrylate] ₃	TL 35 4193 (1994)
O ₂ , PhCHO, cat RuO ₂	SL 1037 (1994)
O ₂ , PhCHO, cat Ni(OAc) ₂ ·4H ₂ O	TL 34 3405 (1993)
O ₂ , PhCHO, cat Ni naphthenate	TL 34 3405 (1993)
O ₂ , PhCHO, cat Cu(OAc) ₂ ·H ₂ O	TL 34 3405 (1993)
H ₂ O ₂ , HCO ₂ H	JCS Perkin I 1182 (1978)
H ₂ O ₂ , HOAc	TL 307 (1970) JOC 37 2363 (1972)
H ₂ O ₂ , HOAc, NaOAc	JCS Perkin I 1182 (1978)
H ₂ O ₂ , (CF ₃ CO) ₂ O	JACS 77 188 (1955); 107 5717 (1985) Tetr 6 253 (1959)
H ₂ O ₂ , (CF ₃ CO) ₂ O, H ₂ NCONH ₂	SL 533 (1990)
98% H ₂ O ₂ , (CF ₃ CO) ₂ O, Na ₂ HPO ₄	Tetr 37 3981 (1981) JOC 47 3871 (1982)
H ₂ O ₂ , CF ₃ COCF ₃	TL 2741 (1970)

H_2O_2 , H_2SO_4 , Ac_2O	<i>Syn Commun</i> 2 139 (1972) <i>JOC</i> 54 139 (1972)
H_2O_2 , PhSeO_2H	<i>CC</i> 870 (1977)
H_2O_2 , Triton B	<i>JACS</i> 115 3146 (1993)
H_2O_2 , NaOH	<i>JOC</i> 48 3497 (1983)
$\text{Ph}_3\text{CO}_2\text{H}$, NaOH	<i>JACS</i> 110 649 (1988) <i>TL</i> 32 4623 (1991)
$\text{PhC}(\text{Me})_2\text{O}_2\text{Li}$	<i>JACS</i> 112 8490 (1990)
$\text{Me}_3\text{CO}_2\text{Li}$	<i>JACS</i> 112 8490 (1990)
$\text{Me}_3\text{CO}_2\text{K}$, 18-crown-6	<i>JOC</i> 55 1909 (1990)
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \\ \diagdown \\ \text{CH}_3 \end{array}$	<i>JOC</i> 53 1088 (1988)
$\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{C} \begin{array}{l} \diagup \text{O} \\ \diagdown \text{O} \end{array} \\ \diagdown \\ \text{CH}_3 \end{array}$, cat $(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{NbH}(\text{OC}=\text{CPh}_2)$	<i>TL</i> 34 7545 (1993)
RCO_3H	<i>Org Rxs</i> 9 73 (1957) (review)
$\text{CF}_3\text{CO}_3\text{H}$	<i>TL</i> 28 3061 (1987); 29 4333 (1988); 32 1027 (1991) <i>JOC</i> 53 1982 (1988)
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$	<i>JOC</i> 50 2759 (1985) <i>TL</i> 31 6501 (1990) <i>SL</i> 707 (1991) <i>JACS</i> 115 3146 (1993)
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$, NaHCO_3	<i>JCS Perkin I</i> 1182 (1978) <i>JOC</i> 52 3560 (1987); 54 3988 (1989); 56 4714 (1991); 57 4567 (1992); 60 3052, 4940 (1995) <i>TL</i> 28 4773 (1987); 34 7669 (1993) <i>Tetr</i> 50 3235 (1994)
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$, KHCO_3	<i>TL</i> 35 7249 (1994)
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$, cat Li_2CO_3	<i>JOC</i> 52 5700 (1987); 58 6779 (1993)
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$, K_2CO_3	<i>JOC</i> 60 3052, 6208 (1995)
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$, cat TsOH	<i>JOC</i> 50 2489 (1985)
<i>m</i> - $\text{ClC}_6\text{H}_4\text{CO}_3\text{H}$, $\text{CF}_3\text{CO}_2\text{H}$	<i>Syn Commun</i> 19 829 (1989) <i>JOC</i> 59 3575 (1994)
magnesium monoperoxyphthalate hexahydrate	<i>Syn</i> 1015 (1987) <i>JOC</i> 54 3754 (1989) <i>SL</i> 635 (1995)
sodium perborate, $\text{CF}_3\text{CO}_2\text{H}$	<i>Tetr</i> 43 1753 (1987)
oxone, wet alumina	<i>CL</i> 331 (1991)
$(\text{Me}_3\text{SiO})_2$, cat Me_3SiOTf	<i>JOC</i> 47 902 (1982)
$\text{Me}_3\text{SiOSO}_3\text{OSiMe}_3$	<i>JOC</i> 44 4969 (1979); 55 93 (1990)

$(\text{Me}_3\text{SiC}_5\text{H}_4)_2\text{NbH}(\text{OC}\equiv\text{CPh}_2)$

TL 34 7545 (1993)

Acinetobacter TD 63 (enantioselective)

TL 30 3663 (1989)

JOC 55 347 (1990); 57 1306 (1992)

Acinetobacter calcoaceticus NCIB 9871

JOC 55 347 (1990)

(enantioselective)

Acinetobacter NCIB 9871 (enantioselective)

JOC 57 1306 (1992)

cyclohexanone oxygenase, NADPH

JACS 110 6892 (1988)

(enantioselective)

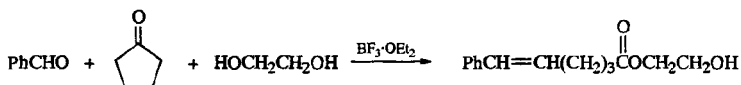


aq KOCl, MeOH

JACS 107 5570 (1985)

NaBr, MeOH, electrolysis

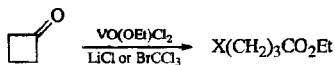
Tetr 47 895 (1991)



CC 1538 (1990); 1482 (1992)

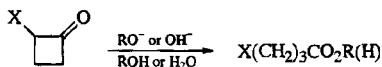
Tetr 47 8523 (1991); 49 10501 (1993)

TL 36 7529 (1995)



X = Cl, Br

JOC 56 2264 (1991)



Review: Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol IV/4, pp 426-430

 $\frac{\text{X}}{\text{Ar}}$

Ar

JACS 97 2218 (1975)

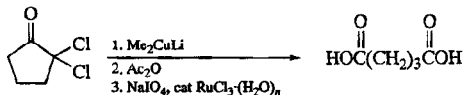
JOC 52 1284 (1987)

TL 29 7175 (1988)

Br₂

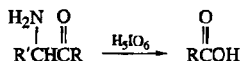
BSCF 763 (1963)

JACS 97 2218 (1975)

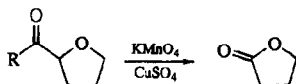


TL 30 7065 (1989)

		$\begin{array}{c} \text{O} \\ \parallel \\ \text{RCCY}_3 \end{array} \longrightarrow \begin{array}{c} \text{O} \\ \parallel \\ \text{RCX} \end{array}$	
<u>X</u>	<u>Y</u>	<u>Reagent(s)</u>	
OH	F	NaH, H ₂ O/HCl	TL 33 2789 (1992)
	Cl	KOH/HCl	Syn Commun 15 711 (1985)
	Cl, Br, I	Y ₂ , OH ⁻	Chakrabarty, "Oxidation in Organic Chemistry," Ed. W. S. Trahanovsky, Pt. C, Academic Press, New York (1978), pp 343-370 (review)
OR	F	NaH, H ₂ O/RX	TL 33 2789 (1992)
	Cl	Na ₂ CO ₃ , MeOH	JACS 105 6755 (1983)
		K ₂ CO ₃ , EtOH	Org Syn Coll Vol 8 254 (1993)
		EtNH ₂ , ROH	JCS Perkin II 175 (1987)
		NaOR, ROH	Ann 755 40 (1972)
NHR	Br	NaOR, ROH	TL 27 2505 (1979)
			JOC 50 425 (1985)
			Ann 755 40 (1972)
	Cl	RNH ₂	JOC 35 4275 (1970); 54 4767 (1989)
			JACS 104 1776 (1982)
			Org Syn Coll Vol 6 1004 (1988)



JACS 110 7447 (1988)

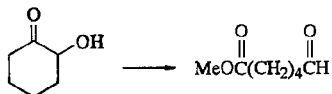


TL 34 1979 (1993)

NaIO₄ JOC 58 2196 (1993)Pb(OAc)₄ JACS 64 1416 (1942)
JOC 54 4083 (1989); 58 2196 (1993)NaBiO₃ JCS 1907 (1950)
JOC 58 2196 (1993)

CAN Syn 560 (1972)

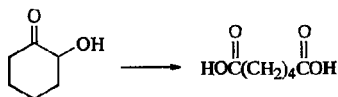
H₂O₂, EDTA JOC 42 4061 (1977)H₂CrO₄ TL 29 6403 (1988)

 H_2IO_6 , MeOH

JOC 55 2694 (1990)

 Pb(OAc)_4 , MeOH

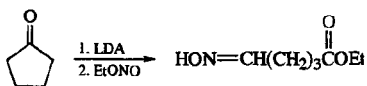
JOC 58 7728 (1993)

 $\text{Ca(OC}_2\text{)}_2$

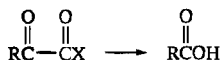
TL 23 3135 (1982)

 O_2 , cat $\text{H}_{3+n}[\text{PMo}_{12-n}\text{V}_n\text{O}_{40}]\cdot\text{H}_2\text{O}$

JOC 58 5663 (1993)



JOC 56 703 (1991)

XReagent(s)

R, ONa

 $\text{Ca(OC}_2\text{)}_2$, H_2O , HOAc, CH_3CN

TL 23 3135 (1982)

R

 HIO_4

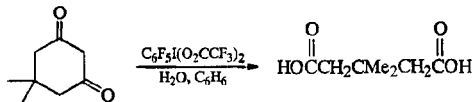
JCS 1467 (1935)

JACS 81 37 (1959)

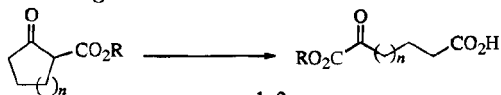
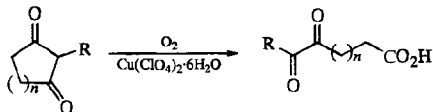
Ph

 $\text{C}_6\text{F}_5\text{I(O}_2\text{CCF}_3)_2$, H_2O , C_6H_6

CC 202 (1987)

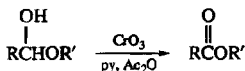


CC 202 (1987)

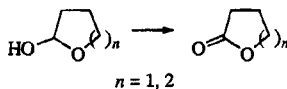
 $n = 1, 2$

TL 35 6089 (1994)

19. Hemiacetals and Lactols



TL 27 3049 (1986)

 Br_2 , CaCO_3 , H_2O

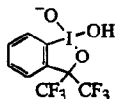
JACS 111 5472 (1989)

 Br_2 , $\text{Ba}(\text{O}_2\text{CPh})_2$, H_2O

TL 28 1073 (1987)

 $\text{H}_2\text{NCONHBr}$

JOC 53 2979 (1988)



JACS 115 6078 (1993)

 CrO_3 , HOAc

TL 27 2757 (1986)

PCC

JACS 105 3720 (1983)

CC 1512 (1985)

TL 26 771 (1985); 27 2757 (1986)

PCC, Al_2O_3

JOC 52 3541 (1987)

PCC, Al_2O_3 , NaOAc

TL 28 6437 (1987)

PCC, NaOAc , molecular sieves

JACS 109 7488 (1987)

PDC, molecular sieves

CC 1714 (1987)

TL 28 5457 (1987)

JOC 57 4888 (1992)

PDC, HOAc , molecular sieves

JACS 109 7534 (1987)

 $\text{Pd}_2(\text{DBA})_3 \cdot \text{CHCl}_3$, $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{OCO}$

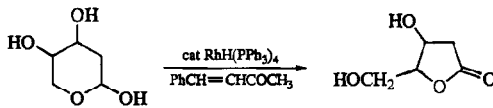
JACS 111 8039 (1989)

 Ag_2CO_3 , Celite

CC 1720 (1987)

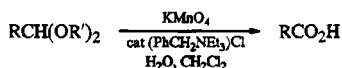
JACS 110 6914 (1988); 112 8100 (1990)

SL 1005 (1992)

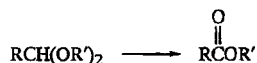



TL 36 383 (1995)

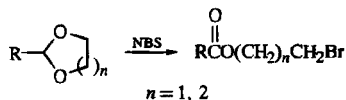
20. Acetals



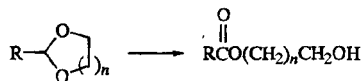
Syn Commun 20 1563 (1990)



O_2	<i>J Gen Chem USSR</i> 58 948 (1988)
$\text{O}_2, h\nu/\text{Na}_2\text{SO}_3$	<i>Ber</i> 91 1935 (1958)
O_3	<i>Can J Chem</i> 52 3651 (1974)
	<i>J Gen Chem USSR</i> 58 948 (1988)
$\text{H}_2\text{O}_2/\text{FeSO}_4$	<i>Ber</i> 94 2722 (1961)
RO_2H	<i>J Gen Chem USSR</i> 58 948 (1988)
<i>t</i> -BuO ₂ H, PDC	<i>JOC</i> 57 5013 (1992)
$(t\text{-BuO})_2$ (R = Ar)	<i>JOC</i> 27 2716 (1962)
	<i>TL</i> 33 4225 (1992)
NBS	<i>JACS</i> 77 4883 (1955)
	<i>TL</i> 1351 (1966)
N_2O_4	<i>J Gen Chem USSR</i> 58 948 (1988)

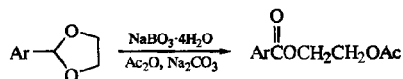


CC 716 (1966)
 TL 1351 (1966)
 Carbohydr Res 2 86 (1966)
 JOC 34 1035 (1969)

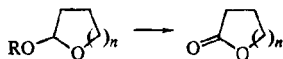


Reagent(s)

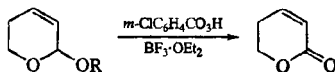
Reagent(s)	n	
O_3	1	<i>Proc Acad Sci USSR, Chem Sec</i> 16 (1987)
<i>t</i> -BuO ₂ H, cat VO(OAc) ₂	1-3	<i>SL</i> 959 (1995)
<i>t</i> -BuO ₂ H, PDC	1, 2	<i>JOC</i> 57 5013 (1992)
<i>t</i> -BuO ₂ H, cat <i>t</i> -BuOPdO ₂ CCF ₃	1-3	<i>CC</i> 1245 (1983)
$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$, Ac ₂ O, Na ₂ CO ₃	1, 2	<i>SL</i> 329 (1995)
KMnO ₄ , (cat PhCH ₂ NEt ₃)Cl, H ₂ O, CH ₂ Cl ₂	1, 2	<i>Syn Commun</i> 20 1563 (1990)



SL 329 (1995)

 n **Reagent(s)**

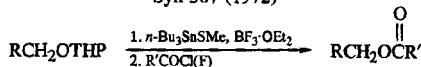
- | | | |
|---|--|--|
| 1 | $m\text{-ClC}_6\text{H}_4\text{CO}_2\text{H}$, $\text{BF}_3 \cdot \text{OEt}_2$ | TL 419 (1978)
JACS 109 7534 (1987)
SL 803 (1993) |
| | H_2CrO_4 | |
| 2 | CrO_3 , HOAc , H_2O | JOC 57 7133 (1992) |
| | H_2CrO_4 | TL 27 2703 (1986); 28 671 (1987) |



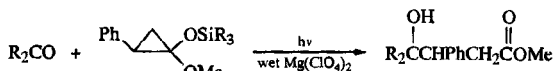
TL 23 3781 (1982)
CC 1714 (1987)



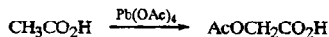
Syn 567 (1972)



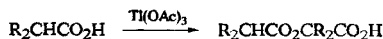
TL 30 1665 (1989)



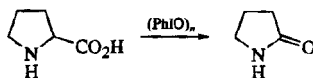
JOC 60 3065 (1995)

21. Carboxylic Acids

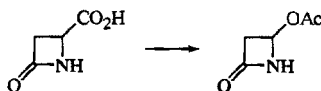
JOC 16 533 (1951)



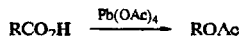
TL 5285 (1970)



TL 29 6917 (1988)



$\text{CH}_3\text{CO}_2\text{H}$, electrolysis	TL 29 1409 (1988)
$\text{CH}_3\text{CO}_3\text{H}$, cat Ru-C	JACS 112 7820 (1990)
$\text{Pb}(\text{OAc})_4$	TL 23 2293 (1982); 31 1921 (1990)
$\text{Pb}(\text{OAc})_4$, $\text{Cu}(\text{OAc})_2$	TL 26 937 (1985)

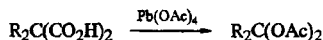


Org Rxs 19 279 (1972) (review)

TL 549 (1976); 27 5319 (1986); 28 781, 4143, 4147 (1987); 33 6949 (1992); 36 983 (1995)

CC 1797 (1987)

JOC 53 1786 (1988); 59 3775 (1994)

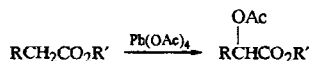


Org Rxs 19 279 (1972) (review)



R'	Reagents	
H	$\text{Pb}(\text{OAc})_4 / \text{H}_3\text{O}^+$	JACS 62 1597 (1940)
Me, Et	NIS, $\text{R}'\text{OH}$	JOC 52 3165 (1987)

22. Esters



HOAc, DDQ ($\text{R} = \text{Ar}$)

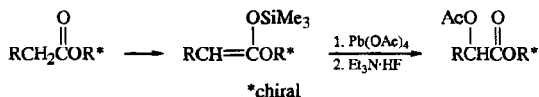
TL 30 325 (1989)

$\text{Pb}(\text{OAc})_4$

Proc Acad Sci USSR, Chem Sec 129 995 (1959)

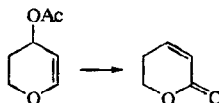
TL 2769 (1970) (lactones)

Syn 567 (1973) (review)



*chiral

Helv 68 216 (1985)



PCC

Carbohydr Res 98 139 (1981)

TL 29 1255 (1988)

PCC, $\text{BF}_3 \cdot \text{OEt}_2$

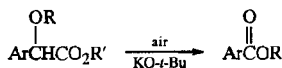
TL 23 3781 (1982)

CrO_3 , $\text{BF}_3 \cdot \text{OEt}_2$

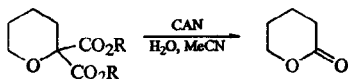
TL 23 3781 (1982)

$m\text{-ClC}_6\text{H}_4\text{CO}_3\text{H}$, $\text{BF}_3 \cdot \text{OEt}_2$

TL 23 3781 (1982)

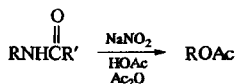


TL 33 5205 (1992)



TL 29 769 (1988)

23. Amides

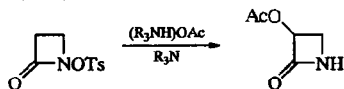


JACS 77 6011, 6014 (1955); 79 2893 (1957); 83 1174, 1179 (1961)

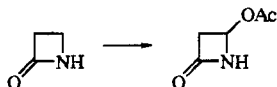
TL 29 4449 (1988)

Tetr 45 863 (1989)

JOC 54 5996 (1989)



JACS 115 548 (1993)

 $\text{CH}_3\text{CO}_2\text{H}$, $n\text{-Bu}_4\text{NBF}_4$, electrolysis

TL 29 1409 (1988)

 $\text{CH}_3\text{CO}_2\text{H}$, NaOAc, CH_3CHO , O_2 , cat
 $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$

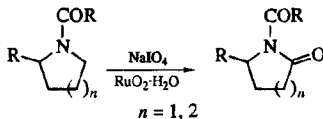
TL 32 5991 (1991)

 $\text{CH}_3\text{CO}_3\text{H}$, cat Ru-C

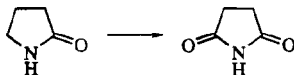
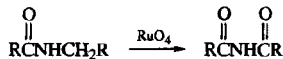
JACS 112 7820 (1990)

 $\text{CH}_3\text{CO}_3\text{H}$, $\text{CH}_3\text{CO}_2\text{H}$, NaOAc, cat OsCl_3

TL 32 2145 (1991)

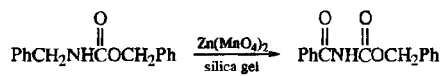


CC 71 (1975)

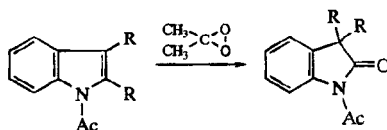


JACS 80 6682 (1958)

TL 31 7403 (1990)

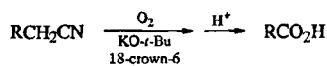


JACS 105 7755 (1983)



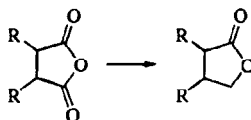
JACS 115 8869 (1993)

24. Nitriles



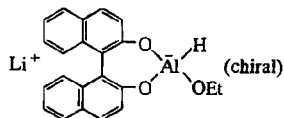
JOC 45 3630 (1980)

2. REDUCTION

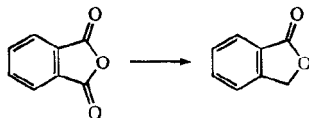


$\text{LiH}_3\text{BCRR}'\text{CN}$ ($\text{R}, \text{R}' = \text{H}, \text{H}; \text{H}, \text{Ph}; \text{Me}, \text{Me}$)

JOC 55 4464 (1990)



TL 34 1167 (1993)

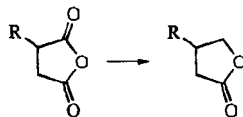


$\text{LiH}_3\text{BCRR}'\text{CN}$ ($\text{R}, \text{R}' = \text{H}, \text{H}; \text{H}, \text{Ph}; \text{Me}, \text{Me}$)

JOC 55 4464 (1990)

$\text{LiH}_2\text{InPh}_2$

TL 36 3169 (1995)



$\text{Na}, \text{C}_2\text{H}_5\text{OH}$

JCS 478 (1936)

$\text{Zn}, \text{HCl}, \text{HOAc}$

Austral J Chem 22 2635 (1969)

TL 33 4061 (1992)

NaBH_4

JOC 35 558, 3574 (1970); 36 2397 (1971); 60 560 (1995)

TL 4651 (1976); 695 (1979); 23 651 (1982); 24 2733 (1983); 28 451, 455 (1987); 33 4061 (1992); 34 1111, 7557 (1993)

JCS Perkin I 2037 (1977)

Can J Chem 56 1524 (1978) (review); 58 2484 (1980)

CC 458 (1982)

JACS 108 4943 (1986)

SL 333 (1993); 186 (1995)

LiHBEt₃

JOC 45 1 (1980)

Heterocycles 18 265 (1982)

LiAlH₄

JOC 32 3919 (1967); 35 558 (1970); 36 2397 (1971)

TL 3589 (1968); 695 (1979)

Can J Chem 56 1524 (1978) (review); 58 2484 (1980)

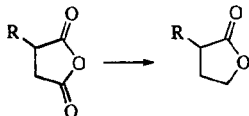
JCS Perkin I 62 (1979)

NaAlH₄

JOC 36 2397 (1971)

LiHAl(*i*-Bu)₂(*n*-Bu)

JOC 49 1717 (1984) (phthalide only)

H₂, cat Ru(II), Et₃N

CC 412 (1975); 314 (1976)

BCSJ 57 897 (1984)

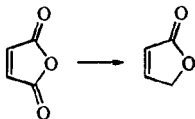
TL 27 365 (1986)

LiHB(*sec*-Bu)₃

Heterocycles 18 265 (1982)

LiHB(Sia)₃

Heterocycles 18 265 (1982)

NaBH₄

Can J Chem 58 2484 (1980)

CC 458 (1982)

KHB(*sec*-Bu)₃

CC 458 (1982)

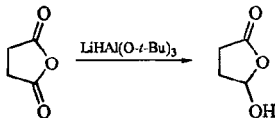
LiAlH₄

JCS Perkin I 62 (1979)

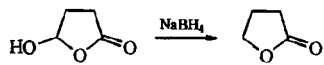
Can J Chem 58 2484 (1980)

LiHAl(O-*t*-Bu)₃

JCS Perkin I 62 (1979)



JOC 35 558 (1970); 36 2397 (1971)



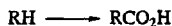
JOC 55 4683 (1990)

3. CARBONYLATION, CARBOXYLATION AND RELATED REACTIONS

Review: H. M. Colquhoun, D. J. Thompson, M. V. Twigg, "Carbonylation-Direct Synthesis of Carbonyl Compounds," Plenum, New York (1991)

See also page 403, Section 6, for the synthesis of α,β -unsaturated nitriles, carboxylic acids and derivatives, and page 1711, Section 4, for the homologation of carbonyl compounds.

1. Carboxylic Acids



CO, HF, SbF₅

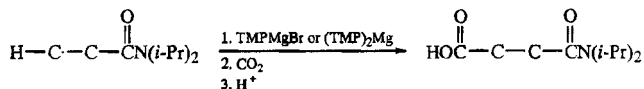
CL 17 (1983)

JACS 110 1303 (1988)

CO, FSO₃H, SbF₅, Cu₂O

BCSJ 49 3335 (1976)

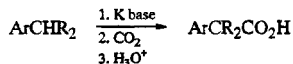
JACS 110 1303 (1988)



(cyclopropanes or cyclobutanes)

JACS 111 8016 (1989)

TL 32 2173 (1991)



JACS 85 3984 (1963)

SL 119 (1991)

See also page 88, Section 2.1.

CO, Pd(OAc)₂

CC 220 (1980)

CO, cat Pd(OAc)₂, *t*-BuO₂H, H₂C=CHCH₂Cl

JOMC 256 C35 (1983)

CO₂, cat Pd(OAc)₂, *t*-BuO₂H

JOMC 266 C44 (1984)

ClCOCOC₂H₅, (AlCl₃)/H₂O

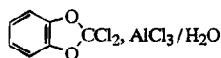
Ber 41 3558 (1908); 44 202 (1911); 45 1186 (1912)

JACS 70 1079 (1948)

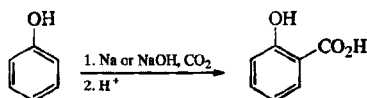
Org Syn 44 69 (1964)

Cl₃CCOCl, AlCl₃/OH⁻

Syn Commun 15 711 (1985)



Ber 96 1382 (1963)



Kolbe-Schmitt reaction

Org Syn Coll Vol 2 557 (1943)

Monatsh 81 1071 (1950)

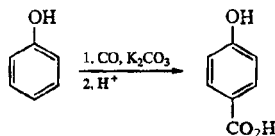
JCS 3145 (1954)

JOC 19 510 (1954); 56 4525 (1991)

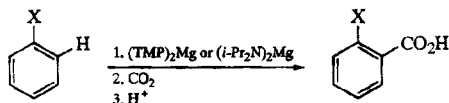
Chem Rev 57 583 (1957) (review)

J Chem Eng Data 14 388 (1969)

Org Prep Proc Int 13 426 (1981)

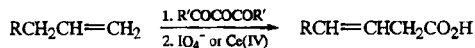


JOC 33 4512 (1968)

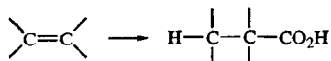
X = CO₂R, CONR₂

JACS 111 8016 (1989)

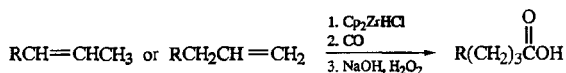
See also page 88, Section 2.1.



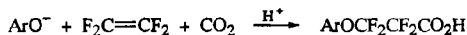
See page 236, Section 8 and page 1859, Section 17.



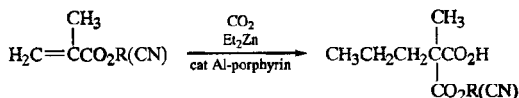
- CO, BF₃, H₂O JACS 70 3793 (1948)
 CO, Fe(CO)₅, OH⁻, H₂O, *i*-PrOH TL 34 2759 (1993)
 CO, NiCl₂ or Ni(CO)₄ Ann 582 53 (1953)
 CO, cat PdCl₂, CuCl₂, O₂, HCl CC 1270 (1983)
 CO, cat PdCl₂, CuCl₂, O₂, HCl, chiral ligand JACS 112 2803 (1990)
 CO, HCO₂H or HO₂CCO₂H, cat Pd-C, cat dppe JOC 58 4739 (1993)
 CO, HCO₂H, cat Pd(OAc)₂(dppe) JOC 58 3595 (1993)
 9-BBN/CO, KHB(O-*i*-Pr)₃/H₂O₂, NaOAc/AgNO₃, NaOH CC 1273 (1982)
 HCO₂H, H₂SO₄ JOC USSR 2 256 (1966)



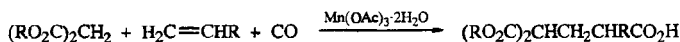
JACS 97 228 (1975)



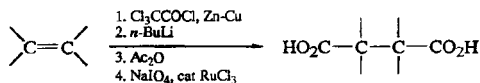
JOC 56 146, 151 (1991)



JACS 113 8492 (1991)

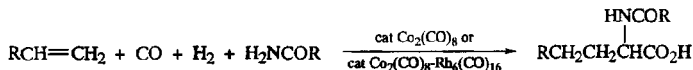


JACS 115 7543 (1993)



JOC 50 1972, 3943 (1985)

Org Syn Coll Vol 8 377 (1993)

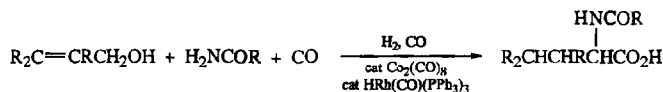


CC 1540 (1971)

JOMC 279 203 (1985)

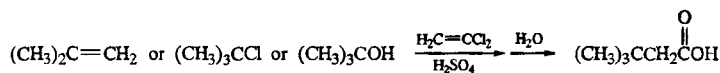
JACS 110 150 (1988)

JOC 54 4511 (1989)



TL 23 2491 (1982)

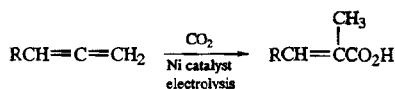
JOMC 279 203 (1985)



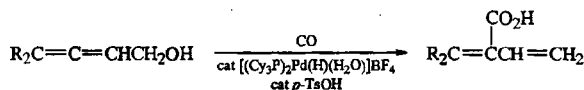
Angew Int 4 956 (1965); 5 870 (1966); 19 171 (1980) (review)

CL 1107 (1980)

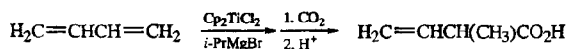
Acta Chem Scand B 34 621 (1980)



SL 361 (1990)



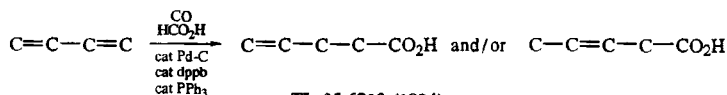
JOC 59 1956 (1994)



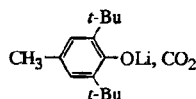
CC 180, 342 (1981)

JOMC 224 327 (1982)

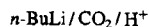
TL 36 5595 (1995) (chiral)



TL 35 6203 (1994)

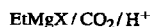


JOC 38 4086 (1973)

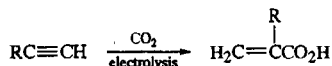


JACS 101 5364 (1979)

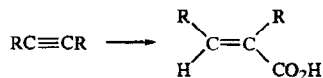
TL 29 6409 (1988)



JACS 65 2208 (1943)

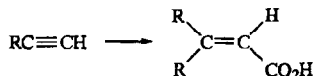


cat NiBr_2 , $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{NMe}_2$	SL 143 (1990)
cat $\text{NiBr}_2(\text{DME})$	JOMC 353 C51 (1988)
cat $\text{Ni}(\text{BF}_4)_2(\text{bipy})_3$	JOMC 352 239 (1988)

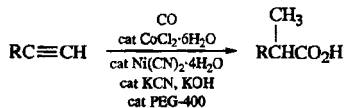


CO_2 , electrolysis, cat NiBr_2 , $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMeCH}_2\text{CH}_2\text{NMe}_2$	SL 143 (1990)
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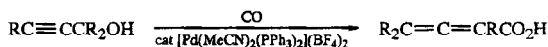
See also page 420, Section 2.6; page 427, Section 2.9; page 447, Section 2.25; and page 448, Section 2.26.



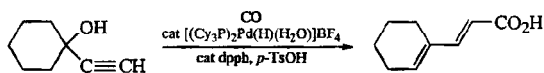
See page 452, Section 2.28.



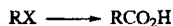
TL 32 1769 (1991)



TL 35 5889 (1994)



JOC 58 6956 (1993)



CO , CoCl_2 , NaBH_4 , NaOH/H^+	TL 28 2633 (1987) ($\text{R} = 1^\circ$ benzylic)
CO , cat $\text{Co}(\text{CO})_3\text{NO}$, NaOH , C_6H_6 , ($n\text{-C}_{12}\text{H}_{25}\text{NMe}_3$)Cl	JOMC 212 C23 (1981) ($\text{R} = 1^\circ$ benzylic)
CO , cat $\text{NaCo}(\text{CO})_4$, NaOH , C_6H_6 , ($\text{PhCH}_2\text{NMe}_3$)Cl	JOMC 134 C15 (1977) ($\text{R} = 1^\circ$ benzylic)
CO , $\text{Co}_2(\text{CO})_8$, NaOH , $h\nu/\text{H}^+$	TL 22 1013 (1981) ($\text{R} = \text{aryl, vinylic}$)
CO , cat $\text{Co}_2(\text{CO})_8$, H_2O , tetramethylurea	JOC 56 4320 (1991) ($\text{R} = 1^\circ$ alkyl)
CO , cat $\text{Co}_2(\text{CO})_8$, H_2O , molecular sieves	TL 32 4733 (1991) ($\text{R} = 1^\circ$ alkyl)
CO , cat $\text{Co}_2(\text{CO})_8$, H_2O , KF	JOC 56 4996 (1991) ($\text{R} = 1^\circ$ alkyl)
CO , cat $\text{Co}_2(\text{CO})_8$, NaOH , C_6H_6 , ($\text{PhCH}_2\text{NEt}_3$)Cl	JOMC 134 C11 (1977) ($\text{R} = 1^\circ$ benzylic)

CO, cat $\text{Co}_2(\text{CO})_8$, KOH, <i>n</i> -BuOH, $(\text{PhNMe}_3)\text{Br}$	JOMC 232 59 (1982) (R = 2° benzylic)
CO; cat $\text{Co}_2(\text{CO})_8$, $\text{Rh}_6(\text{CO})_{16}$ or $\text{PdCl}_2(\text{PPh}_3)_2$; H_2O ; base	TL 30 4403 (1989) (R = $\text{R}'\text{CH}_2\text{CHR}$)
CO, cat $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$, NaOH, PhMe, $(n\text{-C}_{16}\text{H}_{33}\text{NMe}_3)\text{Br}$	JOC 53 5147 (1988) (R = aryl) TL 30 2615 (1989) (R = vinylic)
CO, cat $\text{Ni}(\text{CN})_2 \cdot 4\text{H}_2\text{O}$, cat $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, NaOH, PhMe, $(n\text{-C}_{16}\text{H}_{33}\text{NMe}_3)\text{Br}$	JACS 111 927 (1989) (R = 1° benzylic)
CO, cat $\text{Pd}(\text{OAc})_2$, cat PPh_3 , KOAc, KI	TL 36 87 (1995) (R = vinylic)
CO, cat $\text{Pd}(\text{OAc})_2$, H_2O , Et_3N , PPh_3	JACS 116 3125 (1994) (R = aryl)
CO, cat PdCl_2 , cat PPh_3 , $\text{Ca}(\text{O}_2\text{CH})_2$	JOC 53 624 (1988) (R = aryl)
CO, cat $\text{PdCl}_2(\text{PPh}_3)_2$, H_2O , tetramethylurea	JOC 56 4320 (1991) (R = 2° alkyl)
CO, cat $\text{PdCl}_2(\text{PPh}_3)_2$, H_2O , molecular sieves	TL 32 4733 (1991) (R = 1°, 2° alkyl; 1° benzylic; aryl)
CO, cat $\text{PdCl}_2(\text{PPh}_3)_2$, H_2O , <i>n</i> -Bu ₃ N	JOC 46 4614 (1981) (R = aryl)
CO, cat $\text{PdCl}_2(\text{PPh}_3)_2$, KF, H_2O	JOC 56 4996 (1991) (R = 1°, 2° alkyl)
CO, cat $\text{PdCl}_2(\text{PPh}_3)_2$, <i>n</i> -Bu ₄ NI, NaOH	JOMC 121 C55 (1976) (R = 1° benzylic, aryl, vinylic)
CO, cat $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{Ca}(\text{OH})_2$, MeOH	TL 28 2721 (1987) (R = aryl)
CO, cat $\text{Pd}(\text{PPh}_3)_4$, NaOH, CH_2Cl_2 or C_6H_6	Organomet 1 775 (1982) (R = 1° benzylic)
CO, cat $\text{Pd}(\text{dppe})_2$, NaOH, <i>t</i> -AmOH, $(\text{PhCH}_2\text{NEt}_3)\text{Cl}$	Organomet 2 801 (1983) TL 24 2965 (1983) (both R = vinylic)
CO, cat $\text{Pd}[\text{i-Pr}_2\text{P}(\text{CH}_2)_3\text{P}(\text{i-Pr})_2]_2$, H_2O , NaOAc	JACS 111 8742 (1989) (ArCl)
CO_2 , electrolysis	TL 36 3345 (1995) (R = 1° allylic)
CO_2 , cat $\text{NiCl}_2(\text{dppe})$, electrolysis	JOMC 264 273 (1984) (R = aryl) JACS 113 2819 (1991) (R = aryl)
CO_2 , cat $\text{NiCl}_2(\text{dppp})$, electrolysis	Nouv J Chim 10 119 (1986) (R = 2° benzylic)
CO_2 , cat Pd, electrolysis	CL 169 (1986) JACS 114 7076 (1992) (both R = aryl)
$\text{RLi}/\text{CO}_2/\text{H}^+$	JACS 108 806, 1311 (1986) (both R = aryl); 112 876 (R = cubane), 8902 (R = aryl) (1990); 114 10775 (1992) (R = aryl) JOC 54 1013 (1989) (R = aryl); 55 5404 (1990) (R = 1° alkyl); 58 3148 (1993) (R = cyclopropyl); 59 5930 (R = aryl), 5987 (R = vinylic) (1994); 60 4412 (1995) (R = aryl) TL 35 6117 (1994) (R = aryl)
$\text{Mg}/\text{CO}_2/\text{H}^+$	Org Syn Coll Vol 1 361 (2° RCl), 524 (3° RCl) (1941); 3 553 (1955) (ArBr); 6 845 (1988) (3° RCl)

JOC 18 432 (1953) (2° RCl, 2° benzylic Cl)

Org Syn 59 85 (1980) (3° RCl)

Syn 587 (1982) (1° RCl)

TL 23 3901 (1982) (1°, 2° allylic Cl)

SL 593 (1° allylic Cl), 992 (2° RCl) (1992)

Ba/CO₂/H⁺

SL 593 (1992)

JACS 116 6130 (1994)

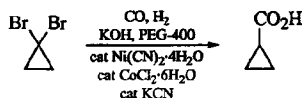
(both R = 1° allylic)

(RS)₃CLi/hydrolysis or esterification

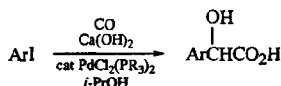
Angew Int 6 442 (1967)

Ber 105 487 (1972)

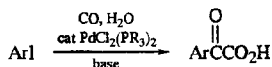
(both R = 1°, 2° alkyl)



TL 32 3349 (1991)



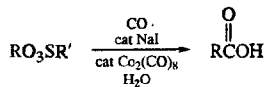
TL 28 2721 (1987)

BaseEt₃N

CC 837 (1985)

Ca(OH)₂

J Mol Catal 41 379 (1987)



R = 1° alkyl; R' = Me, o-Tol

TL 32 3091 (1991)

CO, cat Pd(OAc)₂, cat dppf, KOAc

TL 33 3939 (1992)

CO₂, cat PdCl₂(PPh₃)₂, electrolysis

CC 1729 (1992)

CO, cat Pd(OAc)₂, n-Bu₃N, cat dppf

JACS 110 1985 (1988)

JOC 59 406 (1994)

CO, cat Pd(OAc)₂, (Et₃NH)O₂CH, PPh₃

TL 26 1109 (1985); 35 835 (1994)

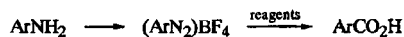
JOC 56 1481 (1991)

CO, cat Pd(OAc)₂(PPh₃)₂, KOAc

TL 33 3939 (1992)

CO, cat Pb₂(DBA)₃·CHCl₃, KOAc

TL 36 87 (1995)

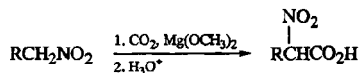
ReagentsCO, cat Pd(OAc)₂, NaOAc/H₂O

TL 21 2877 (1980)

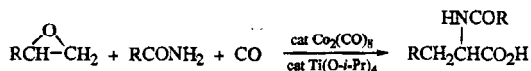
JOC 45 2365 (1980)

CO, cat CuCl₂, H₂O

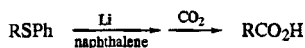
SL 596 (1990)



JACS 81 505 (1959); 85 616 (1963)



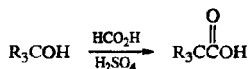
JOMC 279 203 (1985)



JOC 43 1064 (1978)

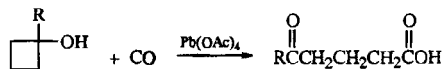
JACS 107 196 (1985)

Tetr 42 2803 (1986)

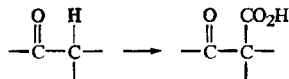


Org Syn Coll Vol 5 739 (1973)

JOC 53 4978 (1988)



SL 1009 (1994)

CO₂, DBU/H⁺

CL 427 (1974)

CO₂, MgCl₂, NaI, CH₃CN, Et₃N/H⁺

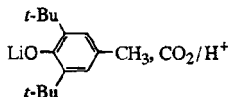
JOC 50 4877 (1985)

CO₂, Mg(OCH₃)₂/H⁺

JACS 81 2598 (1959)

JOC 31 1747 (1966); 38 2489 (1973) (lactone); 52 1686 (1987)

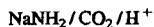
Tetr 38 2797 (1982) (lactone)



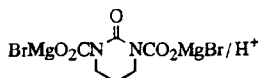
JOC 38 4086 (1973)

LiN(SiMe₃)₂/CO₂/H⁺

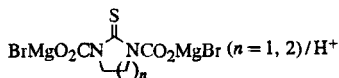
JACS 111 3728 (1989)



JACS 66 1768 (1944); 106 4186 (1984)

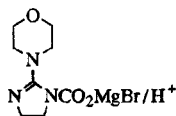


TL 21 1967 (1980)



CC 1487 (1983)

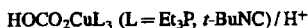
JACS 110 1985 (1988)



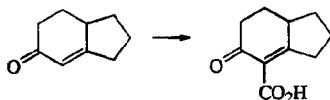
CC 326 (1980)



BCSJ 55 3949 (1982)



JACS 102 431 (1980)

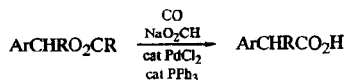


JOC 38 3239 (1973)

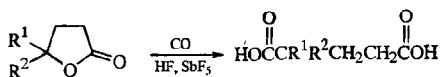


JACS 107 7184 (1985)

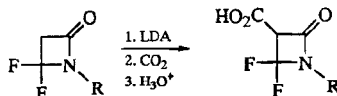
JOC 58 3938 (1993)



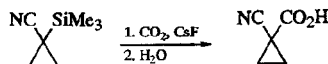
JOC 56 1928 (1991)



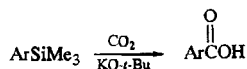
CC 767 (1981)



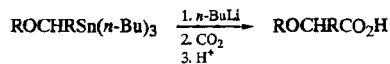
JOC 58 245 (1993)



SL 919 (1991)



Angew Int 20 265 (1981)



TL 37 1983 (1990)

MReagentsTe-*n*-Bu*n*-BuLi / CO₂ / H₃O⁺

TL 36 7625 (1995)

HgCl

PdCl₂, LiCl, CO, H₂O

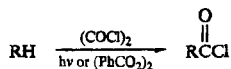
JOC 40 3237 (1975)

cat PdCl₂ or Pd-C, LiCl, CuCl₂, H₂O

JOC 40 3237 (1975)

For M = Cu, see page 452, Section 2.28.

2. Acid Halides

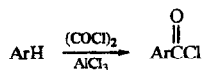


JACS 62 454 (1940); 64 329, 1621 (1942)

JOC 32 197 (1967); 33 1448, 2108 (1968); 35 369 (1970); 43 2399 (1978); 59 2132 (1994); 60 698 (1995)

TL 1605 (1969); 36 1233 (1995)

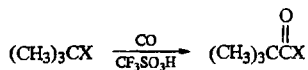
Angew Int 32 612 (1993)



Nature 162 526 (1948)

JCS 520 (1949)

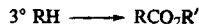
Org Syn Coll Vol 7 420 (1990)



X = Cl, Br

TL 29 4569 (1988)

3. Esters

HF-SbF₅ / CO / R'OH

TL 30 701 (1989)

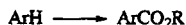
HCO₂H, H₂SO₄, R''OH / R'OH

J Gen Chem 33 3206 (1963)

JOC USSR 1 1596 (1965); 2 256 (1966)

(COCl)₂, hv / R'OH

TL 36 1233 (1995)

*n*-BuLi / ClCO₂Et

JACS 106 3286 (1984)

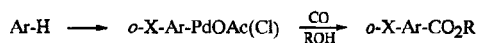
$\text{Ti}(\text{O}_2\text{CCF}_3)_3 / \text{CO}$, cat Li_2PdCl_4 , ROH

JOC 45 363 (1980); 59 383 (1994)

JACS 104 1900 (1982)

$\text{ClCOCCl}_3 / \text{NaOEt}$

JOC 50 425 (1985)



$\frac{\text{X}}{\text{NHCOR}}$

CHNR'_2

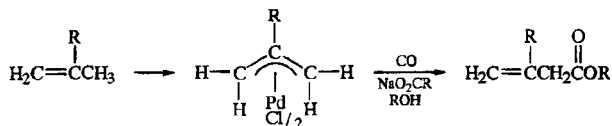
JOC 46 4416 (1981)

JOMC 182 537 (1979)

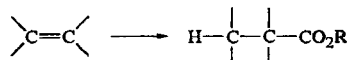
BCSJ 52 142, 957 (1979)

$\text{CH}_2\text{CH}_2\text{NMe}_2$

TL 27 1971 (1986)



Organomet 1 888 (1982)



CO , ROH, cat $\text{Co}_2(\text{CO})_8$

JOC 57 4189 (1992)

CO , ROH, HCl, cat Pd-clay

JOC 60 250 (1995)

CO , ROH, cat $\text{PdCl}_2(\text{PPh}_3)_2$

JOC 53 4422 (1988); 57 4189 (1992)

TL 33 3667 (1992)

CO , ROH, cat $\text{PdCl}_2(\text{CyPPH}_2)_2$

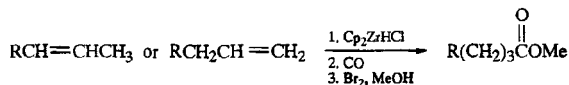
SL 569 (1991)

HCO_2H , $\text{H}_2\text{SO}_4 / \text{ROH}$

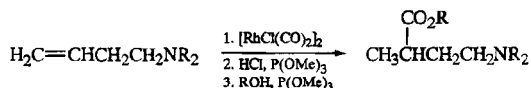
JOC USSR 1 1814 (1965); 2 256 (1966)

PhSeCO_2R , $n\text{-Bu}_3\text{SnH}$

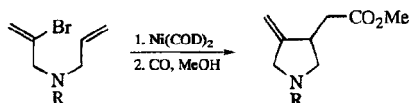
TL 31 227 (1990)



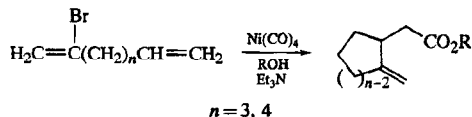
JACS 97 228 (1975)



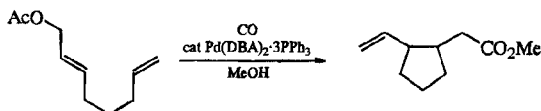
TL 29 6421 (1988); 30 539 (1989)



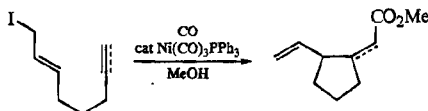
JACS 116 12133 (1994)



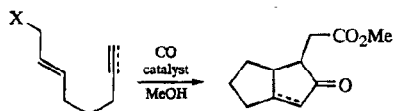
TL 33 3683 (1992); 35 4011 (1994)



TL 30 5883 (1989); 31 6877 (1990)



TL 29 6433 (1988); 30 5883 (1989)



X

Catalyst

I

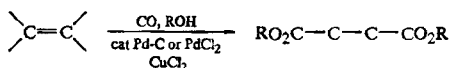
Ni(COD)-dppb

TL 30 5883 (1989)

OAc

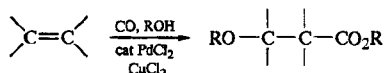
Pd(dba)₃·3PPh₃

TL 30 5883 (1989)

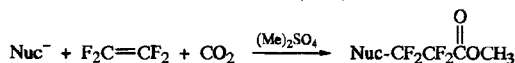


JACS 98 1810 (1976)

JOC 57 6075 (1992)

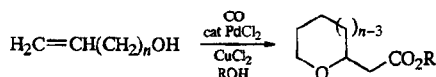


JACS 98 1810 (1976)

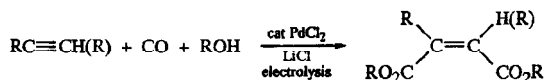
Nuc⁻ = Cl⁻, RO⁻, ArO⁻, RS⁻, N₃⁻, CN⁻, (RO)₂P(O)⁻

JACS 106 5544 (1984)

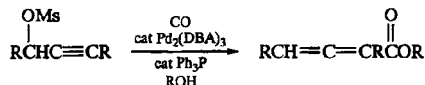
JOC 56 146, 151 (1991)



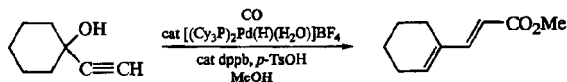
See page 889, Section 2.



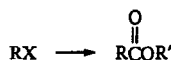
TL 34 8067 (1993)



JOC 60 796 (1995)



JOC 58 6956 (1993)



X = halogen

CO; MeOH: cat $\text{Mn}_2(\text{CO})_{10}$, $\text{Co}_2(\text{CO})_8$, $\text{Ru}_3(\text{CO})_{12}$, TL 29 3833 (1988) $\text{Re}_2(\text{CO})_{10}$ or $\text{Os}_3(\text{CO})_{12}$; K_2CO_3 ; hv (R = 2° alkyl)CO, cat $\text{Fe}(\text{CO})_5$, R_4NX , $\text{R}'\text{OH}$ (R = 1° alkyl, 1° allylic, 1° benzylic), JOC 54 2475 (1989)CO, $\text{R}'\text{OH}$, cat $\text{Co}(\text{OAc})_2$, NaH, *t*-AmOH, hv (R = aryl, vinylic), JOC 60 8336 (1995)CO, $\text{R}'\text{OH}$, cat $\text{Co}_2(\text{CO})_8$, molecular sieves (R = 1° alkyl), TL 32 4733 (1991)CO, $\text{R}'\text{OH}$, cat $\text{Co}_2(\text{CO})_8$, tetraalkylurea (R = 1° alkyl), JOC 56 4320 (1991)CO, $\text{R}'\text{OH}$, cat $\text{Co}_2(\text{CO})_8$, Et_3N (R = 1° alkyl), JOC 56 4996 (1991)CO; $\text{R}'\text{OH}$: cat $\text{Co}_2(\text{CO})_8$, $\text{ClRh}(\text{PPh}_3)_3$, $\text{Rh}_6(\text{CO})_{16}$ or PdCl_2L_2 (R = $\text{R}'\text{CH}_2\text{CHR}$), TL 30 4403 (1989)CO, $\text{M}(\text{OR}')_4$ (M = Ti, Zr), cat $[\text{ClRh}(\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)]_2$ (R = benzylic), JOC 50 2134 (1985)CO, $\text{HCO}_2\text{R}'$, cat $[\text{ClRh}(\text{H}_2\text{C}=\text{CHCH}_2\text{CH}_2-\text{CH}=\text{CH}_2)]_2$, cat KI (R = 1° alkyl; 1°, 2° benzylic), CC 167 (1986)CO, $\text{HCO}_2\text{R}'$, cat $[\text{ClRh}(\text{H}_2\text{C}=\text{CHCH}_2-\text{CH}_2\text{CH}=\text{CH}_2)]_2$, cat $\text{Pd}(\text{PPh}_3)_4$, cat KI (R = aryl), CC 167 (1986)CO, $\text{R}'\text{OH}$, Pd catalyst (R = benzylic, aryl, vinylic, heterocyclic), JOC 39 3318 (1974); 40 532 (1975); 47 3630 (1982); (2-methylene-4-alkanolide); 57 1262 (1992)

- BCSJ 48 2075, 2091 (1975)
 JACS 98 5832 (1976); 102 4193 (1980)
 TL 133 (1979) (2-alken-4-olide); 21 3885 (1980); 23 4361 (1982); 32 157 (1991); 36 8715 (1995)
 Heterocycles 12 921 (1979) (3*H*-isobenzofuran-1-one, isochroman-1-one, 4,5-dihydro-3*H*-benzo-[*c*]oxepin-1-one)
 CL 369 (1980)
 JCS Perkin I 1706 (1989)
- CO, ArOH, cat PdCl₂, cat dppp, base (R = aryl) SL 515 (1994)
- CO, R'OH, cat PdCl₂(PPh₃)₂, molecular sieves (R = 1°, 2° alkyl; benzylic; aryl) TL 32 4733 (1991)
- CO, R'OH, cat PdCl₂(PPh₃)₂, tetraalkylurea (R = 2° alkyl, benzylic, vinylic, aryl) JOC 56 4320 (1991)
- CO, R'OH, cat PdCl₂(PPh₃)₂, KF or Et₃N (R = 1° alkyl) JOC 56 4996 (1991)
- CO, R'OH, NaOAc, cat Pd[i-Pr₂P(CH₂)₃P(i-Pr)₂]₂ (RX = ArCl) JACS 111 8742 (1989)
- CO, HCO₂R', NaOR', cat PdCl₂(PPh₃)₂ (R = aryl, vinylic) TL 32 4705 (1991); 33 2001 (1992); 35 4995 (1994)
- CO, Ti(OR')₄, cat Pd(PPh₃)₄ (R = 1° alkyl, aryl, vinylic) JOC 50 2134 (1985)
- CO, Zr(OR')₄, cat Pd(PPh₃)₄, cat [CIRh(H₂C=CHCH₂CH₂CH=CH₂)₂] (R = aryl, vinylic) JOC 50 2134 (1985)
- CO, MeOH, cat PtCl₂(PPh₃)₂, K₂CO₃, (hv) (R = 1°, 2° alkyl; aryl; vinylic; alkynyl) CC 351 (1986)
 TL 29 3833 (1988)
 JOC 54 1831 (1989)
- CO, MeOH, cat Pt(CO)₂(PPh₃)₂, base, (hv) (R = 1°, 2°, 3° alkyl; vinylic; alkynyl) TL 29 3833 (1988)
 JOC 54 1831 (1989)
- Fe(CO)₅, NaOR' (R = 1° alkyl) CL 1355 (1977)
- Na₂Fe(CO)₄/(CO)/I₂, R'OH (R = 1° alkyl) JACS 95 249 (1973); 111 3382 (1989)
- Ni(CO)₄, R'OH, (Et₃N) (R = vinylic) JOC 54 3334 (1989)
 TL 33 3683 (1992)
- Ni(CO)₄, NaOR' (R = 1° alkyl, aryl, vinylic) JACS 91 1233 (1969); 92 6314 (1970); 104 6646 (1982)
- (Ph₃P)₂Ni(CO)₂, R'OH, Et₃N (R = vinylic) JACS 104 6879 (1982) (2-methylene-4-alkanolide)
 TL 34 4485 (1993)
- Li or Mg/MnI₂/ClCO₂Et (R = 1° alkyl, aryl, vinylic) BSCF 570 (1977)
- n*-BuLi/ClCO₂Me (R = vinylic) JACS 110 4741 (1988)
- t*-BuLi/ClCO₂Me (R = aryl) JACS 115 7593 (1993)
- Mg/ClCO₂Et (R = aryl) Ber 36 3087 (1903)

Mg/OC(OEt)₂ (R = aryl) Org Syn Coll Vol 2 282 (1943)

Mg/NCC(OEt)₃/H₃O⁺ (R = 1°, 2° alkyl; aryl) TL 22 1509 (1981)

Mg/Fe(CO)₅/I₂, R'OH (R = 1° alkyl, aryl) TL 1477 (1978)

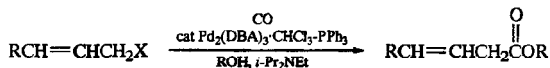
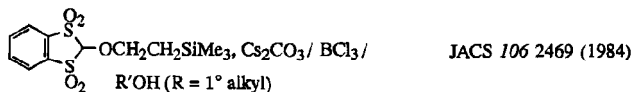
LiC(OMe)(SiMe₃)₂/electrolysis (R = 1° alkyl) TL 30 219 (1989)

LiC(OMe)₂CN/H₃O⁺ (R = 1° alkyl) TL 22 4279 (1981)

LiC(SMe)₃/HgCl₂, HgO, MeOH (R = 1° allylic) JOC 59 4853 (1994)

NaOH, MeSCH₂SO₂Me/SOCl₂/MeOH
(R = 1° alkyl, benzylic, allylic) TL 22 4499 (1981)

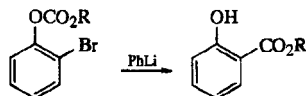
NaOH, MeSCH₂SO₂Tol (phase transfer)/H₂O₂,
HOAc/MeOH, H⁺ (R = 1° alkyl, benzylic,
allylic) CL 767 (1983)



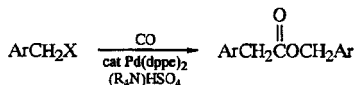
X = Cl, Br, O₂CR, OCO₂R, OPO(OR)₂

TL 29 4945 (1988); 35 4389 (1994)

JOC 58 1538 (1993)

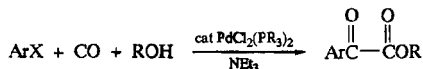


TL 35 1749 (1994)



X = Cl, Br

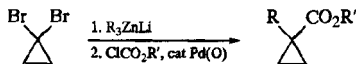
Organomet 1 775 (1982)



CL 567 (1985)

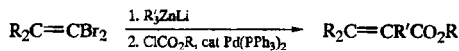
J Mol Catal 32 115 (1985); 34 317 (1986)

JOC 52 5733 (1987)

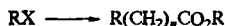


TL 30 6039 (1989)

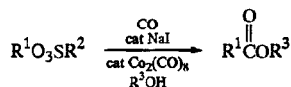
JOC 58 2958 (1993)



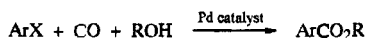
JOC 58 4897 (1993)

 $n = 1, 2$; X = halogen

See page 1724, Section 2.

 $R^2 = \text{Me}, o\text{-Tol}$

TL 32 3091 (1991)

X

OTf

TL 27 3931 (1986); 33 5499 (1992); 34 1615 (1993);
35 6985, 9189 (1994); 36 7035 (1995)

CC 904 (1987)

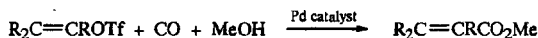
SL 405 (1991); 49 (1995)

JOC 59 6902 (1994); 60 5069, 5899 (1995)

OSO₂F

TL 33 1959 (1992)

JOC 59 6683 (1994)

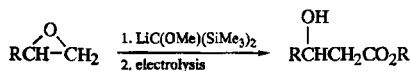


TL 26 1109 (1985); 29 2793 (1988)

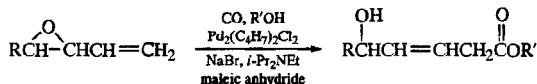
CC 1002 (1987)

JOC 53 227 (1988); 54 3334, 5148, 5828 (1989); 55 3004, 5711 (1990); 56 1481 (1991); 57 3274, 5979
(1992); 59 406, 1216, 5419 (1994); 60 2656, 8126 (1995)

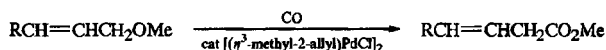
JACS 111 8039 (1989); 113 7424, 9384 (1991); 114 2567, 7387 (1992)



TL 30 219 (1989)



TL 34 2135 (1993)

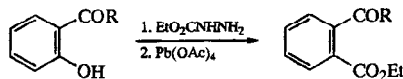


JOC 54 2459 (1989)

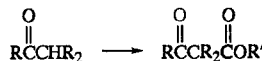


NaI, ethylpolyphosphate, cat $\text{Co}_2(\text{CO})_8$, *n*-Bu₃N BCSJ 55 643 (1982)

H₂S, H₂O, cat $\text{Co}_2(\text{CO})_8$ JOC 53 3306 (1988)



TL 31 6781 (1990)



LDA / CO_2 / CH_2N_2 JACS 108 800 (1986)

$\text{KN}(\text{SiMe}_3)_2$ / CO_2 / CH_2N_2 JACS 102 889 (1980)

chiral $\text{LiN}(\text{CHPhMe})_2$ / CO_2 / MeI
(enantioselective) TL 27 2767 (1987)

$\text{LiN}(\text{SiMe}_3)_2$ / ClCO_2Me JACS 113 5765 (1991)

LDA / $\text{NCCO}_2\text{R}'$ TL 24 5425 (1983); 26 2291 (1985); 28 1051 (1987);
31 4755 (1990)

JACS 109 2850 (1987)

SL 169 (1990)

JOC 57 4386 (1992)

(Li)NaN(SiMe₃)₂ / NCCO_2Me JACS 107 2730 (1985)

TL 28 3985 (1987)

MeLi / NCCO_2R (on enol silane) TL 26 5433 (1985)

NaOMe, $\text{OC}(\text{OMe})_2$ JACS 107 7967 (1985)

NaH / $\text{OC}(\text{OR})_2$ JACS 69 2677 (1947); 70 2287 (1948); 75 4287
(1953)

Chem Ind 576 (1956)

Org Syn Coll Vol 5 198 (1973)

Chem Pharm Bull 30 2590 (1982)

JOC 59 6313 (1994)

NaH, cat KH, $\text{OC}(\text{OMe})_2$ Syn Commun 6 169 (1976)

Org Syn Coll Vol 7 351 (1990)

NaNH_2 / $\text{OC}(\text{OEt})_2$ JACS 66 1768 (1944); 67 2197 (1945)

KO-*t*-Bu / $\text{OC}(\text{OEt})_2$ BSCF 543 (1959)

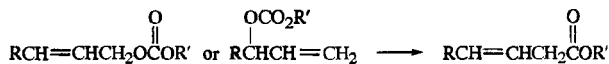
NaO-*t*-Am, CS_2 / MeI / MeOH, $\text{BF}_3 \cdot \text{OEt}_2$, HgO Syn Commun 12 829 (1982)



$\text{ClCO}_2\text{R}'$, DMAP JOC 52 5425 (1987)

LDA / $\text{NCCO}_2\text{R}'$ TL 27 1221, 1225, 1229 (1986) (all lactones); 28
1051, 1725 (1987)

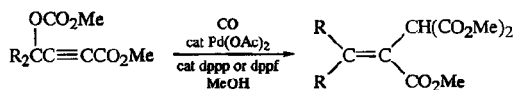
JACS 110 5442 (1988); 112 2749 (1990)

CO, cat $\text{Ru}_3(\text{CO})_{12}$, cat 1,10-phenanthroline

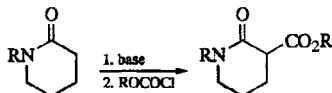
JOC 59 7759 (1994)

CO, cat $\text{Pd}(\text{OAc})_2$, cat PPh_3

TL 23 5189 (1982)

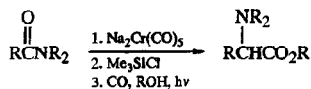


TL 35 5697, 5701 (1994)

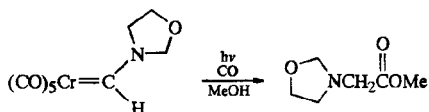


TL 28 4901 (1987)

JACS 110 5927 (1988)

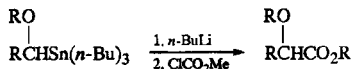


JACS 112 2264 (1990)

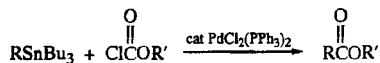


JACS 114 2991 (1992); 115 87 (1993)

JOC 57 6914 (1992) (intramolecular)



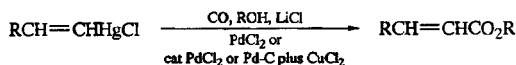
TL 31 1985 (1990)



R = aryl, vinylic

Organomet 10 366 (1991)

SL 117 (1993)

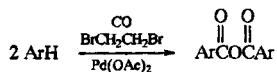


JOC 40 3237 (1975)

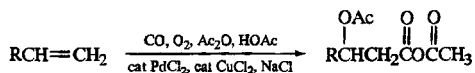
4. Lactones

See page 1861, Section 8.

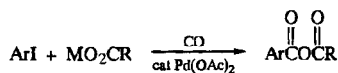
5. Acid Anhydrides



CC 132 (1982)

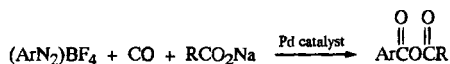


TL 29 4435 (1988)



M = Na, K, Ca

JOC 54 36 (1989)



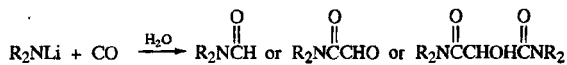
TL 21 2877 (1980)

JOC 46 4413 (1981)

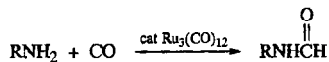
6. Amides

Review: Org Prep Proc Int 22 269 (1990)

See also page 1861, Section 8.



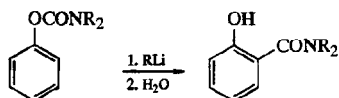
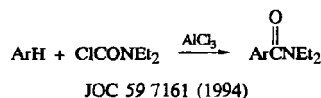
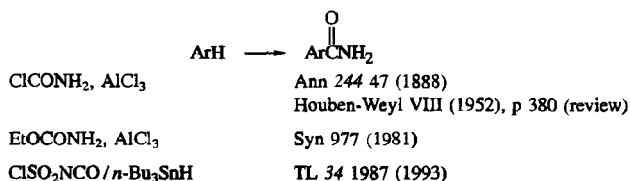
JOC 58 1847 (1993)



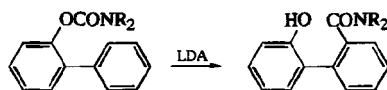
JOMC 309 333 (1986)



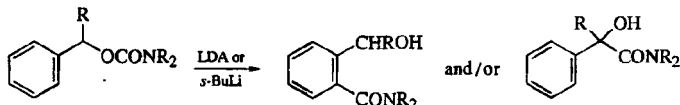
JOMC 236 C53 (1982)



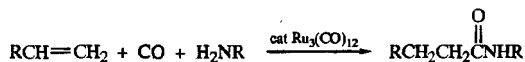
JOC 48 1935 (1983)
 JACS 107 6312 (1985); 111 4829 (1989)



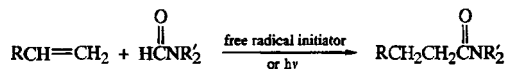
JOC 57 424 (1992)



JOC 58 3223 (1993)

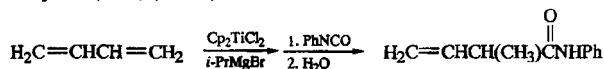


JOMC 309 333 (1986)



$\text{R}' = \text{H, Me}$

Angew 73 621 (1961)
 Chem Ind 362 (1962)
 JOC 29 1855 (1964); 30 3361 (1965); 31 3829 (1966); 55 1500 (1990)
 Z Chem 4 177 (1964)
 Syn 99 (1970) (review)



CC 342 (1981)
 JOMC 224 327 (1982)

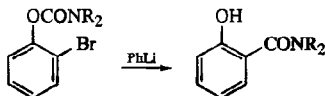
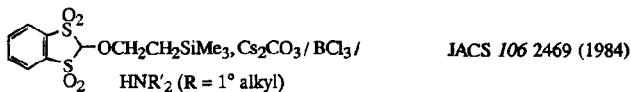
	$\text{RC}\equiv\text{CH} \longrightarrow \text{RC}\equiv\text{CCNR}'_2$	
RLi/R'NCO/H ₂ O		Ann 1844 (1981)
ClCONMe ₂ , cat PdCl ₂ (PPh ₃) ₂ , cat CuI, Et ₃ N		Syn 777 (1977)
	$\text{RC}\equiv\text{CH} + \text{CO} + \text{R}_2\text{NH} \longrightarrow \text{H}_2\text{C}=\text{C}(\text{R})\text{C}(\text{R})\text{NR}_2$	
cat PdCl ₂ (PPh ₃) ₂ , cat PPh ₃ , cat MeI		CL 1673 (1991)
cat Pd(OAc) ₂ , cat P(O- <i>i</i> -Pr) ₃ , cat Et ₃ NMe·HI		SL 409 (1993)
	$\text{RC}\equiv\text{CH} \longrightarrow \begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{C} \begin{array}{l} \text{H} \\ \diagup \end{array} \\ \diagup \quad \diagdown \\ \text{R} \quad \text{CONHR} \end{array}$	
	See page 452, Section 2.28.	
	$\text{RX} \longrightarrow \text{RCNR}'_2$	
	X = halogen	
CO, HNR' ₂ , Pd catalyst (R = aryl, vinylic)		JOC 39 3327 (1974); 43 1684 (1978) (2,3-dihydro-isoindol-1-one, 3,4-dihydro-2H-isoquinolin-1-one, 2,3,4,5-tetrahydrobenzo[c]azepin-1-one); 57 6351 (1992)
		BCSJ 48 2091 (1975)
		Heterocycles 6 1711, 1841 (1977) (3,4-dihydro-2H-isoquinolin-1-one)
		Syn Commun 10 523 (1980)
		CC 741 (1982) (2,3,4,5-tetrahydrobenzo[c]azepin-1-one)
		Chem Pharm Bull 32 3840 (1984) (2,3,4,5-tetrahydrobenzo[c]azepin-1-one)
		JACS 107 4577 (1985)
		TL 35 4677 (1994)
CO, HNR' ₂ , cat Pd[<i>i</i> -Pr ₂ P(CH ₂) ₃ P(<i>i</i> -Pr) ₂] ₂ (RX = ArCl)		JACS 111 8742 (1989)
CO, R' ₃ N, cat PhPdI(PPh ₃) ₂ (R = aryl, vinylic)		JOMC 231 C12 (1982)
CO, HNR' ₂ , cat Pt(CO) ₂ (PPh ₃) ₂ , K ₂ CO ₃ (R = 2° alkyl)		TL 29 3833 (1988)
Ni(CO) ₄ , HNR' ₂ (R = vinylic)		JACS 91 1233 (1969)
Li[(CO) ₃ NiCONMe ₂] (R = aryl, benzylic, allylic, vinylic)		JOC 36 2721 (1971)
LiCu(CONR' ₂) ₂ (R = aryl, allylic)		JOC 44 3734 (1979)
Li/Mg(OCH ₂ CH ₂ OEt) ₂ /HCONR ₂ /PhCOPh (R = 1° alkyl, 1° benzylic, aryl)		JOC 53 5151 (1988)
<i>n</i> -BuLi / ClCONEt ₂ (R = aryl)		JACS 109 3402 (1987)
		JOC 59 7161 (1994)
Mg / LiOCH ₂ CH ₂ OEt / HCONR ₂ / PhCHO or Ph ₂ CO (R = 1°, 2° alkyl; aryl)		JOC 53 5151 (1988)

Mg/PhNCO/H₂O (R = 2° alkyl, 2° benzylic) JOC 18 441 (1953)

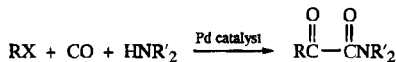
Mg/Cp₂TiCl₂, PhNCO/H₂O (R = 1°, 2° alkyl in RX; R = 1° alkyl in RCONR'₂) TL 28 3815 (1987)

Mg, *t*-BuNCO, ultrasound/H₂O (R = aryl) TL 27 501 (1986)

EtOCH(Me)OCH(CN)₂, K₂CO₃/CF₃CO₂H/R'₂NH JOC 55 4515 (1990)
(R = 1° alkyl)



TL 35 1749 (1994)



R = aryl, vinylic; X = halogen

JOMC 233 C64 (1982)

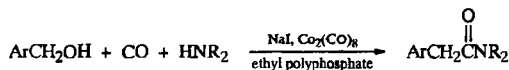
TL 23 3383 (1982); 30 4407 (1989) (R = R_yCH₂CHR)

CL 865 (1982)

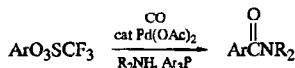
Organomet 3 683, 692 (1984)

JACS 106 1506 (1984); 107 3235 (1985)

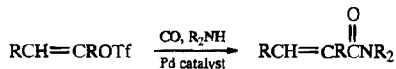
JOC 51 415 (1986)



BCSJ 55 643 (1982)

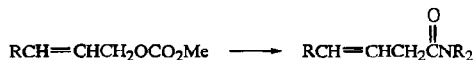


TL 27 3931 (1986)



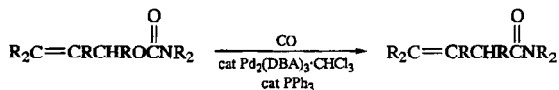
TL 26 1109 (1985); 28 6117 (1987); 29 3785 (1988); 34 255 (1993)

JACS 113 5085 (1991); 115 3966 (1993)

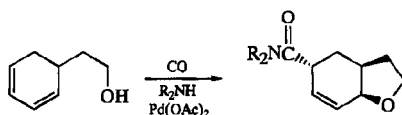


CO, cat Ru₃(CO)₁₂, cat 1,10-phenanthroline, R₂NH JOC 59 7759 (1994)

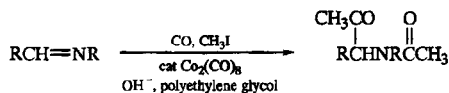
EtOCH(Me)CH(CN)₂, cat Pd₂(DBA)₃·CHCl₃, cat PPh₃/CF₃CO₂H/R₂NH JOC 55 4515 (1990)



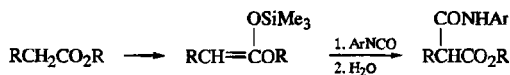
SL 323 (1992)



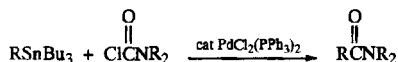
TL 35 4441 (1994)



TL 29 5113 (1988)



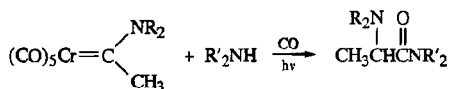
JOMC 164 123 (1979)



R = aryl, vinylic

Organomet 10 366 (1991)

SL 117 (1993)

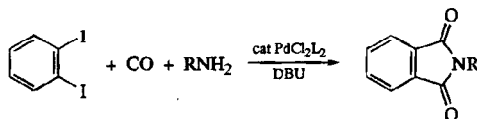


JACS 114 5602 (1992); 115 87, 9037 (1993); 117 3697 (1995)

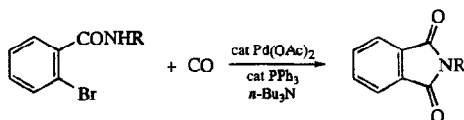
7. Lactams

See page 1861, Section 8.

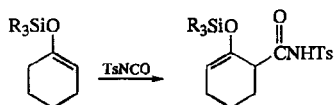
8. Imides



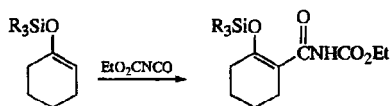
JOC 56 6573 (1991)



Heterocycles 13 329 (1979)



JACS 112 462 (1990)

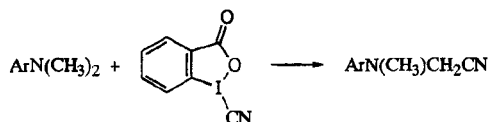


JACS 112 462 (1990)

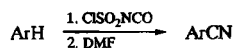
9. Nitriles



SL 821 (1992)



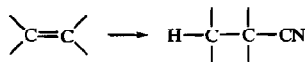
TL 36 7975 (1995)



Org Syn 50 52 (1970)

Org Syn Coll Vol 6 465 (1988)

TL 36 5921 (1995)



Review: E. S. Brown in "Organic Syntheses via Metal Carbonyls," Eds. I. Wender and P. Pino, Wiley Interscience, New York (1977), Vol 2, p 655

HCN, cat $\text{Co}_2(\text{CO})_8$

JACS 76 5364 (1954)

HCN, Ni catalyst

J Catalysis 26 254 (1972)

CC 1098 (1981)

Austral J Chem 35 2041 (1982)

Adv Catalysis 33 1 (1985) (review)

JACS 114 6265 (1992)

HCN, Pd catalyst

CC 112 (1969)

JACS 101 6128 (1979)

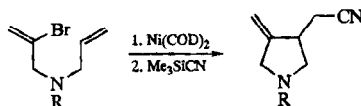
TL 23 1621 (1982)

Austral J Chem 35 2041 (1982)

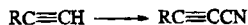
 $\text{Cp}_2\text{ZrHCl/RN}=\text{C}$ ($\text{R} = i\text{-Bu, SiMe}_3$)/ I_2

TL 28 295 (1987)

JOC 56 1192 (1991)



JACS 116 12133 (1994)

CuCN, $(\text{Me}_3\text{SiO})_2$

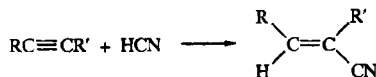
TL 32 2169 (1991)

CuCN, Me_3SiCl , cat NaI, H_2O , DMSO, CH_3CN

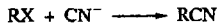
TL 34 5911 (1993)

 $n\text{-BuLi}$ / PhOCN

Syn 150 (1980)



See page 447, Section 2.25 and page 448, Section 2.26.

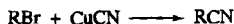
 $\text{R} = 1^\circ, 2^\circ \text{ alkyl}$

Chem Rev 42 189 (1948) (review)

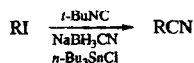
"The Chemistry of the Cyano Group," Ed. S. Patai, Interscience, New York (1970), p 67 (review)

JOC 23 3416 (1974) (18-crown-6); 51 3447 (1986); 54 4476 (phase transfer), 4993 (ion exchange resin)

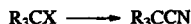
(1989); 56 3102 (1991) (18-crown-6); 59 4853 (1994) (18-crown-6)

 $\text{R} = \text{allylic, propargylic}$

JOC 59 284 (1994)



JOC 53 4855 (1988); 54 3240 (1989)

Me₃SiCN, SnCl₄

Angew Int 20 1017 (1981)

Tetr 39 961 (1983)

Syn 1140 (1985)

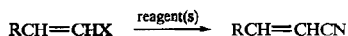
JOC 51 3447 (1986)

Me₃SiCN, TiCl₄ (benzyl chlorides)

JOC 59 3838 (1994)

t-BuLi / (CN)₂

JOC 52 2674 (1987)

XReagent(s)

Cl, Br

Co(CN)₄³⁻KCN, NiBr₂(PPh₃)₂, Zn, PPh₃

JACS 104 1560 (1982)

CL 1565 (1982)

Br

Co(CN)₅³⁻K₄Ni₂(CN)₆, KCNKCN, cat Pd(PPh₃)₄

CuCN

JOC 50 3934 (1985)

JACS 91 1233 (1969)

TL 4429 (1977)

BSCF 720 (1973)

JOC 43 2839 (1978); 52 2674 (1987)

NaCu(CN)₂

JOC 34 3626 (1969)

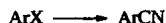
I

CuCN

JOMC 93 415 (1975)

TL 28 6351 (1987)

JOC 59 4143 (1994)



Review: Chem Rev 42 189 (1948)

Reagent(s)XNaCN, cat Ni(PPh₃)₄

Cl, Br, I

JOMC 54 C57 (1973)

NaCN or KCN, cat Ni(PPh₃)₄ or
ArNiCl(PPh₃)₂, phase transfer

Cl, Br

JOMC 173 335 (1979)

NaCN-alumina, cat Pd(PPh₃)₄

Br, I

JOC 44 4443 (1979)

KCN, cat Ni(PPh₃)₄

OTf

JCS Perkin I 1365 (1989)

KCN, cat NiCl₂(PPh₃)₂, cat PPh₃, Zn

OMs

JOC 60 6895 (1995)

KCN, cat NiBr₂(PPh₃)₂, cat PPh₃,
cat Zn

OTf

JCS Perkin I 1365 (1989)

CL 1957 (1989)

TL 31 6321 (1990)

KCN, cat Pd(PPh₃)₄

I

CL 277 (1975)

KCN, cat Pd₂(DBA)₃·CHCl₃,
cat dppf

OTf

CL 1957 (1989)

TL 35 9189 (1994)

KCN, cat Pd(OAc)₂, NaOEt

Br, I

BCSJ 48 3298 (1975)

Me₃SiCN, cat Pd(PPh₃)₄

I

JOC 51 4714 (1986)

n-Bu₃SnCN, cat Pd(PPh₃)₄

I

JACS 111 8502 (1989)

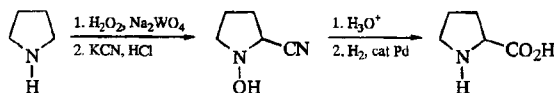
Reagent(s)	X	
CuCN	Cl, Br, I	Org Syn Coll Vol 3 212, 631 (1955) JACS 81 3667 (1959); 94 3080 (1972); 114 9309, 9877 (1992); 117 1514, 5245 (1995) JOC 26 2522, 2525 (1961); 34 3626 (1969); 50 2128 (1985); 51 4169 (1986); 52 3196 (1987); 53 2706 (1988); 56 1747 (1991); 59 2894 (1994) JCS 1097 (1964) Quart Rev 19 95 (1965) TL 33 29 (1991)
CuCN-charcoal	Br	CC 877 (1986)
NaCu(CN) ₂	I	JOC 34 3626 (1969)
Zn(CN) ₂ , cat Pd(PPh ₃) ₄	Br, I	Syn Commun 24 887 (1994) JOC 60 4324 (1995)
Zn(CN) ₂ , cat Pd(OAc) ₂ - <i>o</i> -Tol ₃ P-Et ₂ Zn	Br	JOC 60 4324 (1995)



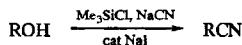
RM	Reagent(s)	
RLi (R = vinylic, alkynyl)	PhOCN	Syn 150 (1980)
RC≡CLi	ClCN	Rec Trav Chim 92 667 (1973)
RC≡CMgX	ClCN	Ann Chim 5 5 (1926) BSCF IV 17 228 (1915)
<i>E</i> -RCH=CHAlMe(<i>i</i> -Bu) ₂	(CN) ₂	JACS 90 7139 (1968)
RCH=CHCu·MgX ₂	ClCN, ArSO ₂ CN	Syn 784 (1977)



Org Syn Coll Vol 1 514 (1941)

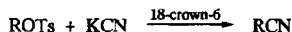


TL 28 6469 (1987)



R = 1°, 2°, 3° alkyl

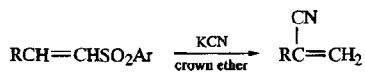
JOC 46 2985 (1981)



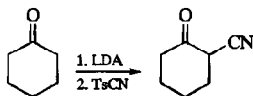
JOC 53 1922 (1988)



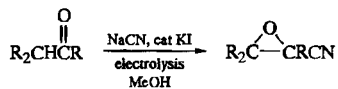
SL 336 (1995)



JOC 46 4817 (1981)



TL 22 5011 (1981)

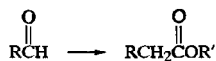


JOC 58 6194 (1993)

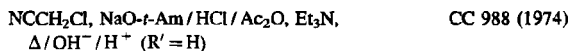
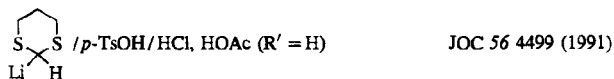
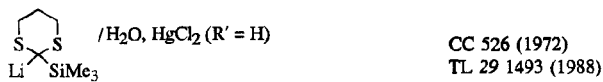
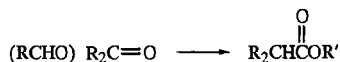
4. CARBONYL HOMOLOGATION AND DEGRADATION

See also page 1861, Section 8.

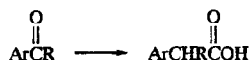
1. Homologation



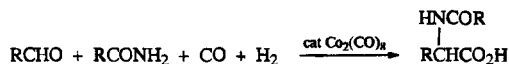
<u>R</u>	<u>Reagents</u>	
aryl	NaC(NMe ₂)[PO(OEt) ₂] ₂ / H ₃ O ⁺ (R' = H) MeSOCH ₂ SMe, base / H ⁺ , R'OH	Angew Int 7 391 (1968) TL 1383 (1972) BCSJ 52 2013 (1979) Chem Pharm Bull 30 2440 (1982) JACS 115 10742 (1993) Syn 1043 (1983)
	ArCONMeCH ₂ CN, NaOH (phase transfer) / H ₃ O ⁺ (R' = H)	
	CBr ₄ , PPh ₃ / OH ⁻ , cat Pd(dppe) ₂ , PEG-400 (R' = H)	JOC 51 4354 (1986)
vinyl	CBr ₄ , PPh ₃ / OH ⁻ , cat Pd(dppe) ₂ , PEG-400 (R' = H)	JOC 51 4354 (1986)



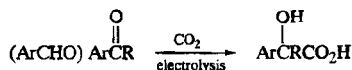
- NCCH_2Cl , $\text{NaO}-t\text{-Am}/\text{LiClO}_4/\text{OH}^-/\text{H}^+$ ($\text{R}' = \text{H}$) CC 988 (1974)
 $\text{PhNMeCH}_2\text{CN}$, $\text{KH}/\text{H}_3\text{O}^+$ ($\text{R}' = \text{H}$) JOC 48 3566 (1983)
 $(\text{EtO})_2\text{POCH}(\text{CN})\text{O}-t\text{-Bu}/\text{Ac}_2\text{O}$, ZnCl_2 , Δ/OH^- or $\text{R}'\text{O}^-$ ($\text{R}' = \text{H}$ or R') JACS 99 182 (1977)
 $\text{Ph}_2\text{POC}(\text{OEt})_2/\text{H}_3\text{O}^+$ ($\text{R}' = \text{H}$) TL 24 1303 (1983)
 JACS 115 459 (1993)
 $\text{Ph}_3\text{P}=\text{CF}_2/\text{R}'\text{OH}-\text{H}_2\text{SO}_4$ or $\text{R}'\text{OH}-\text{Hg}(\text{OAc})_2-(\text{CF}_3\text{CO})_2\text{O}$ CL 651 (1980)
 CBr_4 , PPh_3/OH^- , cat $\text{Pd}(\text{dppe})_2$, PEG-400 JOC 51 4354 (1986)
 ($\text{R}' = \text{H}$)



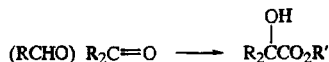
- $\text{Me}_3\text{SiCN}/\text{SnCl}_2/\text{HOAc}/\text{HCl}$ Syn Commun 12 763 (1982)
 CFCl_3 , TiCl_4 , $\text{LiAlH}_4/\text{HCl}$, H_2O TL 34 7973 (1993)

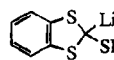


- CC 1540 (1971)
 J Mol Catal 6 341 (1979)



- Angew Int 22 492 (1983)
 CL 453 (1984)
 BCSI 58 1723 (1985)
 TL 27 3429 (1986)
 JOC 60 742 (1995)



- $\text{Me}_3\text{SiCN}/\text{R}'\text{OH}$, HCl JOC 55 2232 (1990)
 $/\text{Hg}(\text{ClO}_4)_2$, MeOH Syn Commun 11 209 (1981)
 ($\text{R}' = \text{Me}$, ketones only)

- $(\text{RS})_3\text{ClLi}/\text{HgCl}_2$, H_2O or MeOH ($\text{R}' = \text{H}$ or Me , aldehydes and ketones) Angew Int 6 442 (1967)
 Ber 105 487 (1972)
 JOC 45 216 (1980)
 TL 22 4009 (1981); 28 475 (1987); 31 1385 (1990)
 JACS 114 6570 (1992)
 $\text{Cl}_2\text{CeC}(\text{SMe})_3/\text{HgCl}_2$, HgO , $\text{R}'\text{OH}$ JOC 57 6861 (1992)

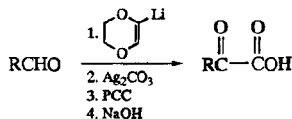
TolSOC(Li)(Cl)R'' / Δ / O₃, H₂O or R'OH
(R' = H or R')

TL 31 3567 (1990)
JOC 56 4129 (1991)

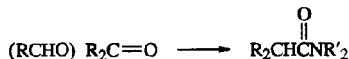
H₂C=C(Li)OEt / O₃ (R' = Et)

JOC 55 5818 (1990); 56 4875 (1991)

See also page 1681, Section 1.



TL 29 6261 (1988)

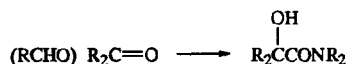


Ph₃P=CF₂ / LiNR'₂ / H₂O (aldehydes only)

CL 935 (1980)

(EtO)₂POCH(CN)O-*t*-Bu / Ac₂O, ZnCl₂, Δ / R'₂NH
(ketones only)

JACS 99 182 (1977)



HCONR₂, base

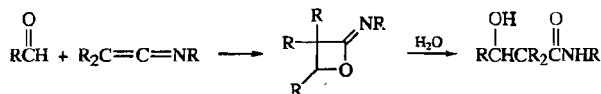
See page 1778, Section 4.

ClCONR₂, Li, cat naphthalene

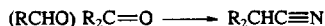
TL 34 7115 (1993)

TolSOC(Li)(Cl)R' / Δ / O₃, R₂NH

TL 31 3567 (1990)
JOC 56 4129 (1991)



JOC 57 5128 (1992)



TsCH₂NC, NaOEt (ketones only)

Syn Commun 2 281 (1972)
JOC 42 3114 (1977)

TsCH₂NC, KO-*t*-Bu

TL 1357 (1973)
Tetr 31 2151, 2157 (1975)
JOC 42 3114 (1977); 55 4497 (1990); 57 6861
(1992); 58 7660 (1993)
Syn Commun 10 399 (1980)
Org Syn Coll Vol 6 41 (1988)

2,4,6-(*i*-Pr)₃C₆H₂SO₂NHNH₂ / KCN, Δ

CC 280 (1977)
JCS Perkin I 1487 (1980)

(EtO)₂POCHN, LiCN / SmI₂, *t*-BuOH

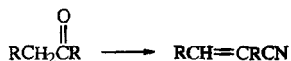
JOC 56 1827 (1991)

H₂NNHCO₂Me / HCN / Br₂ or NBS / NaOMe

TL 3541 (1977)
Org Syn Coll Vol 6 334 (1988)






JOC 55 1070 (1990)



See page 308, Section 54.6.

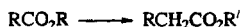


<u>X</u>	<u>Reagents</u>	
OH	 NOH, DCC/PhSO ₂ CH=CH ₂ , hv/ <i>m</i> -ClC ₆ H ₄ CO ₂ H/ (CF ₃ CO) ₂ O/K ₂ CO ₃	TL 32 3309 (1991)
	 NOH, DCC/H ₂ C=C(O ₂ CCF ₃)CN, hv/KOH	TL 33 5013 (1992)
OR, NR ₂	 NOH, DCC/H ₂ C=C(O ₂ CCF ₃)CN, hv/ROH or R ₂ NH	TL 34 6505 (1993)



X = halogen, OPh

JACS 86 1640 (1964)

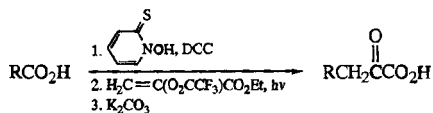


MeSOCHNaSMc/NaBH₄/Ac₂O/R'OH, H⁺ CL 659 (1974)

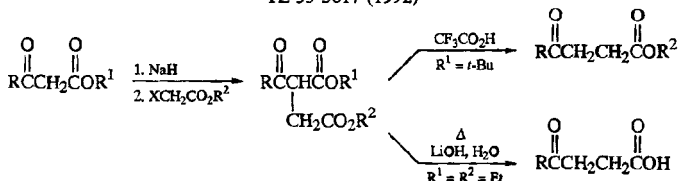
PhSOCHClLi/KH/*t*-BuLi/R'OH (R' = H, Me) TL 35 133 (1994)

LiCHBr₂/*n*- or *t*-BuLi/EtOH (R' = Et) JACS 104 321 (1982); 107 1429 (1985)

LiCHBr₂/LiN(SiMe₃)₂/RLi/R'OH, HCl JOC 57 7194 (1992)

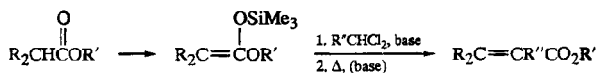


TL 33 5017 (1992)



TL 33 3579 (1992); 34 2051 (1993)

JOC 60 5107 (1995)



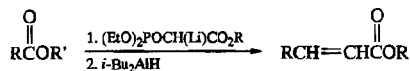
$R'' = H, Me, Ph, F$

Syn 58 (1982)

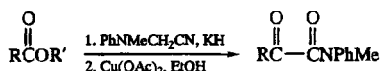
BSCF 455 (1985)

Tetr 41 2643, 2653 (1985)

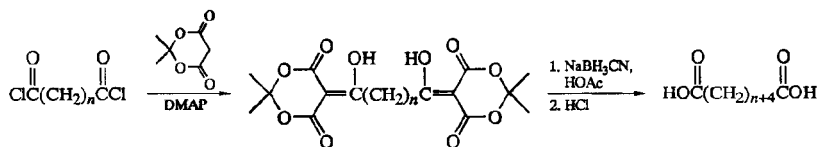
JOC 55 4807 (1990) (lactones)



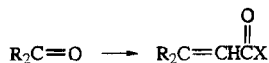
TL 35 2305 (1994)



CL 859 (1983)

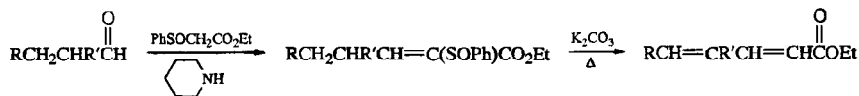


Syn Commun 12 19 (1982)

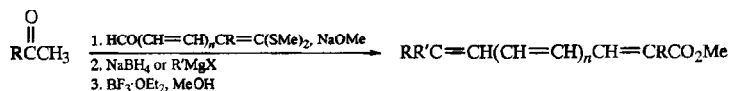


$X = OH, OR, NR_2$

See page 327, Section 4.

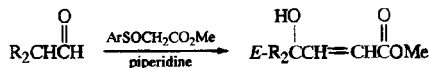


CL 781 (1980)



$R' = H, Me, Ph; n = 1, 3$

TL 31 1763 (1990)



JCS Perkin I 570 (1979)

CC 1248 (1981); 1268 (1986)

CL 1703 (1982)

Syn 134 (1983)

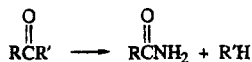
Gazz Chim Ital 115 637 (1985)

TL 30 3633, 4325 (1989); 31 7555 (1990); 32 2409 (1991); 34 8025 (1993)
JOC 56 2050 (1991) (enantioselective)

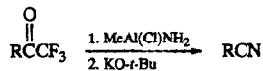


TL 22 4489 (1981); 27 5109 (1986) (enantioselective)
JACS 106 7890 (1984)
Gazz Chim Ital 115 637 (1985)
JOC 56 2050 (1991) (enantioselective)

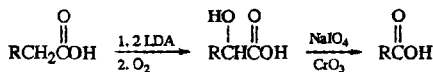
2. Degradation



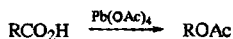
See page 67, Section 12.6.



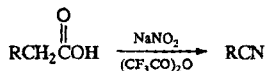
TL 36 4035 (1995)



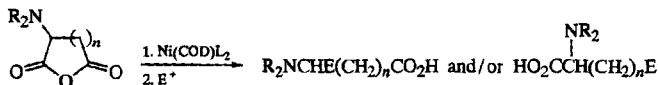
Syn Commun 9 63 (1979)



See page 1672, Section 21.



JOC USSR 11 653 (1975)



$n = 1, 2$; $\text{E}^+ = \text{H}_3\text{O}^+$, DCl , NBS

TL 31 4783 (1990)



R'

Me, Et

$\text{CH}_2\text{CH}=\text{CH}_2$

Reagents

LiCl , H_2O , DMSO

HCO_2H , cat $\text{Pd}(\text{OAc})_2$, cat PPh_3

JOC 53 434 (1988)

TL 32 2409 (1991)

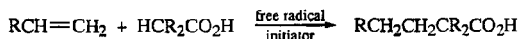
5. ALKYLATION, ACYLATION AND SUBSTITUTION OF NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 1.1, p 1

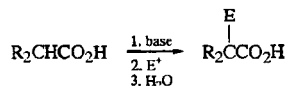
See also page 236, Section 8, for *ene* reactions leading to unsaturated carboxylic acids, esters and amides.

1. Carboxylic Acids

See also page 1724, Section 2.



Syn 99 (1970) (review)
JCS Perkin II 1655 (1973)



Reviews:

Syn 509 (1977); 521 (1982)

P. L. Creger, "Annual Reports in Medicinal Chemistry," Vol 12, Academic Press, New York (1977), Chpt 12

E^+

D_2O

RX

JOC 37 451 (1972)

JCS 1551 (1950)

JACS 78 4942 (1956); 89 2500 (1967); 92 1397 (1970); 103 5459 (1981); 104 5523 (1982); 107 7776 (1985); 109 1186, 7816 (1987); 110 5768 (1988); 112 6690 (1990)

E⁺RX (*continued*)

JOC 26 3696 (1961); 32 2797 (1967); 35 262 (1970); 37 451 (1972); 45 3236 (1980) (stereochemistry); 46 1616 (1981); 47 893 (1982); 50 2719 (1985); 51 1541 (1986); 52 1309, 2549 (1987); 54 2992 (1989); 57 252 (1992); 58 5931 (1993)
 Org Syn 50 58 (1970)
 Syn 517 (1975); 710 (1980)
 Can J Chem 58 716 (1980); 60 1238 (1982)
 Tetr 36 775 (1980)
 TL 27 4545 (1986); 28 2941 (1987); 29 3175 (1988); 36 1071 (1993)
 CC 656 (1987) (chiral base)
 Org Syn Coll Vol 6 517 (1988)

PhCH₂SeCH₂Br

JOC 51 2981 (1986)

epoxide

JACS 89 2500 (1967)
 Can J Chem 58 716 (1980)
 JOC 52 34 (1987)
 TL 34 1597 (1993)

H₂CO

JOC 37 1256 (1972)

RCHO, R₂CO

JACS 74 1730 (1952); 94 2000 (1972); 102 2841 (1980); 117 9653 (1995)
 Compt Rend C 270 1471 (1970)
 BSCF 1848 (1970)
 Israel J Chem 8 731 (1970)
 JOC 36 1149 (1971); 40 8 (1975); 46 3359 (1981); 51 1478 (1986); 52 3143, 4124 (1987); 53 1218, 2134 (intramolecular), 2371, 5922 (1988); 60 7006 (1995) (B enolate)
 CC 52 (1979); 98 (1986)
 Tetr 40 2211 (1984) (enantioselective with chiral bases)
 TL 28 2753, 4787 (1987); 29 4665, 5735 (1988); 36 3679 (1995)
 Org Syn Coll Vol 7 386 (1990)

ArCH=NR

JOMC 231 185 (1982) (zinc enolate)

HCO₂R

TL 699 (1970); 603 (1974)
 JOC 52 4303 (1987)

RCO₂R

JACS 93 6321 (1971); 106 1811 (1984); 116 11275 (1994)

RCOCl

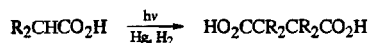
JOC 42 1189 (1977)
 J Chem Res (S) 44 (1980)
 JACS 116 11275 (1994)

EtO₂CCO₂Et

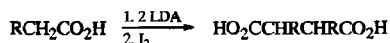
TL 22 2459 (1981)

CO ₂	Israel J Chem 8 731 (1970) JOC 37 451 (1972) Syn 587 (1982)
ClCO ₂ R	SL 827 (1992)
RNCO, RNCS	JOC 45 1106 (1980)
RCH=CHCO ₂ R (1,4-addition)	JACS 93 6321 (1971) TL 34 1323 (1993)
RCH=CHCN (1,4-addition)	JACS 93 6321 (1971)
RCH=CHNO ₂ (1,4-addition)	See page 1511, Section 12.
O ₂	Syn 647 (1971) (hydroxy acid) JOC 40 3253 (1975) (hydroxy or hydroperoxy acid); 41 370 (1976) (hydroperoxy acid)
MeSSMe	JACS 107 8066 (1985)
Me ₃ SiCl	JOC 58 6126 (1993)

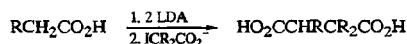
For halogenation, see page 730, Section 4.



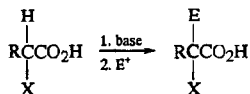
JACS 113 2233 (1991)



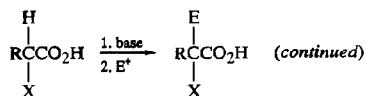
TL 25 5969 (1984); 27 127 (1986); 28 4441 (1987)
JOC 52 2549 (1987); 53 3745, 4724 (1988)



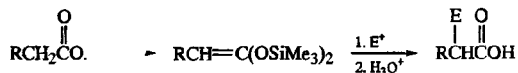
TL 25 5969 (1984)



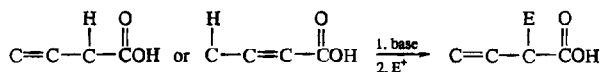
<u>X</u>	<u>R</u>	<u>E</u> ⁺	
Cl	Cl	RX	Syn 115 (1984) JACS 110 5533 (1988)
	Me	R ₂ CO RX, RCOCl (decarboxylation), α,β-unsaturated esters (cyclopropanes)	Syn 115 (1984) Syn 284 (1982)
OPh	H	D ₂ O, RX D ₂ O, RX, RCHO, R ₂ CO epoxide	Syn 828 (1978) JOC 43 772 (1978) TL 2835 (1977)
	OPh	D ₂ O, RX	Syn 828 (1978)



<u>X</u>	<u>R</u>	<u>E</u> ⁺	
OMe	Me	R ₂ CO	Can J Chem 51 981 (1973)
OR	R	RCHO, R ₂ CO	TL 33 6783 (1992)
SMe	CH ₂ CH=CH ₂	RX, RCHO	CL 351 (1982)
SPh	H	epoxide	CL 385 (1974) BCSJ 50 242 (1977) TL 26 5623, 5627, 5631 (1985) JACS 108 5352 (1986) Tetr 43 5055 (1987) JOC 57 4991 (1992)
	H, Me alkyl	RCH=CRNO ₂ (1,4-addition) epoxide	CL 1505 (1982) TL 34 5043 (1993)
SePh	H	epoxide	CC 754 (1986) TL 28 1147 (1987)
N=CHNMe ₂	R	RX	JACS 115 11612 (1993) (as oxazaborolidinone)
NHCOPh	H	D ₂ O, RX epoxide	TL 2205 (1976) JACS 111 1057 (1989)
NHCO ₂ R	H	D ₂ O, RX, H ₂ CO	TL 33 6461 (1992)
CO ₂ R	H	RCOCl	JOC 44 310 (1979) Org Syn 61 5 (1983)
	R	RX	JOC 54 5413 (1989) (chiral)
CN	H	RCOCl	Syn 308 (1983)

E⁺

R ₃ CCl, ZnCl ₂	Ber 116 3708 (1983)
RCHClSPh, ZnBr ₂	TL 23 5083 (1982)
HC≡CCO ₂ Me, TiCl ₄ (E = CH=CHCO ₂ Me)	JACS 107 3879 (1985)
RCH(OR) ₂ or R ₂ C(OR) ₂ , TiCl ₄	TL 30 6109 (1989)
RCHO, TiCl ₄	TL 25 2143 (1984); 29 1275 (1988)
RCH=NR, TiCl ₄ (3-alkanelactam formation)	TL 25 2143 (1984)
Pb(OAc) ₄ (E = OAc)	TL 28 3971 (1987)


 E^+
 H_2O or D_2O

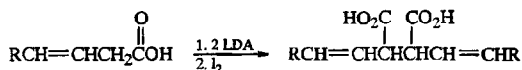
JOC 36 3290 (1971); 52 4471 (1987)
 TL 26 1939 (1985)

 RX

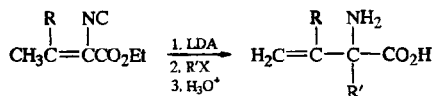
JCS 1551 (1950)
 JACS 93 4330 (1971); 98 4925 (1976)
 JOC 36 3290 (1971); 42 260 (1977); 46 239 (1981);
 52 4471 (1987)
 Gazz Chim Ital 104 625 (1974)
 Tetr 32 1347 (1976)
 TL 335 (1979); 22 1691 (1981); 36 1071 (1995)

 RCHO , R_2CO

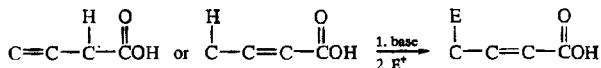
TL 1163 (1973); 22 4913 (1981); 23 4773 (1982); 28
 3853 (1987)
 JCS Perkin I 400 (1973)
 Tetr 32 107 (1976)
 JOC 40 8 (1975); 46 239 (1981); 49 4424 (1984)
 JCS Perkin I 1651 (1978)
 Syn 802 (1985)



TL 33 891 (1992)



Syn 646 (1981)


 E^+
 RX

TL 31 5741 (1990)

 RX , CuI

JACS 98 4925 (1976)
 Tetr 32 1347 (1976)
 CC 500 (1977)
 JOC 46 239 (1981)
 TL 22 1691 (1981)

 RCHO , R_2CO

JOC 29 3161 (1964); 46 2439 (1981); 49 4424
 (1984)
 JACS 90 3282 (1968)
 Compt Rend C 270 1471 (1970)
 BSCF 1848 (1970)

RCHO, R₂CO (continued)

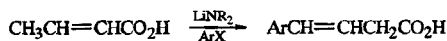
Chem Ind 80 (1972)
 Austral J Chem 25 2393 (1973)
 JCS Perkin I 400 (1973); 1651 (1978); 1597 (1979)
 TL 1163 (1973); 3851 (1974); 22 4913 (1981); 23 4773 (1982); 28 3853 (1987)
 Gazz Chim Ital 103 117 (1973)
 Tetr 32 107 (1976)
 Syn 802 (1985)

H₂C=CHCOR (1,4-addition)

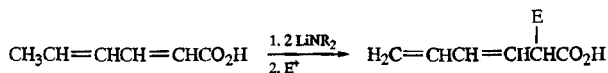
JCS Perkin I 1651 (1978)

$$\text{H}_2\text{C}=\text{CHCH}(\text{O})\text{CH}_2, \text{CuI (1,4-addition)}$$

JOC 46 239 (1981)



JOC 57 667 (1992)

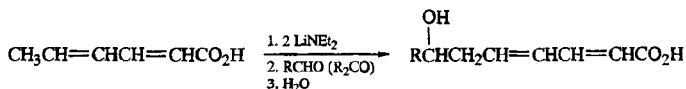
 E^+

RX

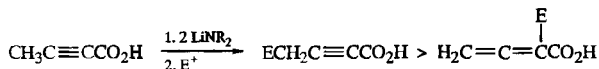
JOC 48 3003 (1983)

RCHO, R₂CO

TL 26 3625 (1985); 33 2465 (1992)



TL 26 3625 (1985); 31 5791 (1990)

 E^+

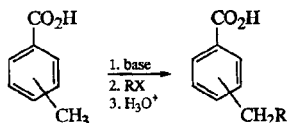
RX

JOC 40 269 (1975)

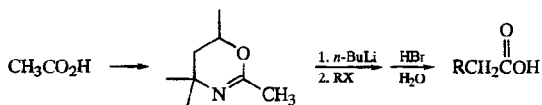
Tetr 32 1347 (1976)

RCHO

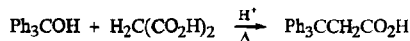
TL 3221 (1975)



JACS 92 1396 (1970)



JACS 91 5886 (1969)



JACS 49 1735 (1927)

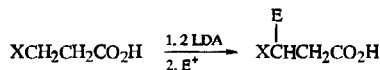
JCS 716 (1962)

TL 34 953 (1993)



TL 2891 (1978)

JOC 55 6356 (1990)


 $\underline{\text{X}}$

SOPh

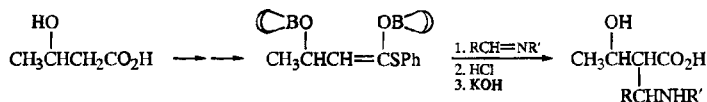
 SO₂Ph

 $\underline{\text{E}^+}$

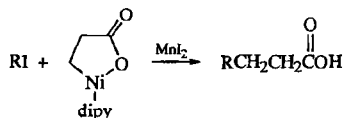
 RX, R₂CO (lactone)

 R₂CO (lactone)

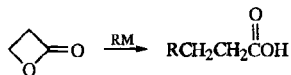
Syn Commun 6 357 (1976)



TL 26 1523 (1985); 27 2149, 2153 (1986)



TL 31 1257 (1990)

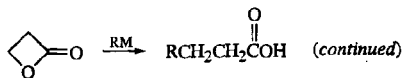

RM

RMgX, cat CuX

TL 21 935, 3377 (1980); 23 3193, 3587 (1982)

CL 571 (1980)

JACS 109 4649 (1987)

RMRMgX, cat Li₂CuCl₄CL 569 (1982)
BCSJ 56 345 (1983)R₂CuLiTL 21 935, 2181 (1980)
JACS 109 4649 (1987)

(RCu≡CR')Li

TL 21 935 (1980)

R₂CuMgXTL 21 935, 2181, 3377 (1980)
CL 1123 (1980)R₂Cu(CN)Li₂

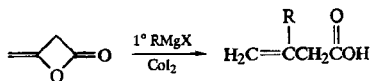
JACS 109 4649 (1987)

RC≡CAI Me₂

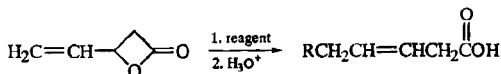
TL 27 87 (1986)

RCdX

JOC 28 2362 (1963)

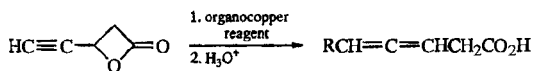


BCSJ 55 3555 (1982)

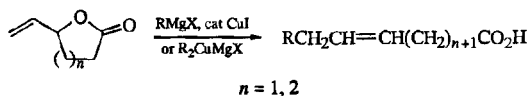
ReagentR₂CuLi or R₂CuMgX or RMgX-cat CuITL 22 1817 (1981)
CL 1307 (1981); 71, 219, 1521 (1982)

LiI (R = I)

CL 71 (1982)

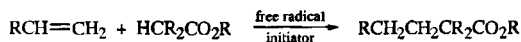


TL 22 2375 (1981)

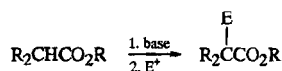


R = 1°, 2°, 3° alkyl; allyl; aryl; vinylic

TL 23 3583, 3587 (1982)

2. Esters

Syn 99 (1970) (review)



Reviews:

Org Rxns 9 107 (1957)

Syn 521 (1982)

 Heterocycles 29 2225 (1989) (E^+ = imines)

 E^+
 H_2O

CC 149 (1985) (stereochemistry)

TL 27 2405 (1986) (lactone, stereochemistry); 28 517 (1987)

 D_2O

JACS 93 2318 (1971)

CC 892 (1972) (lactone)

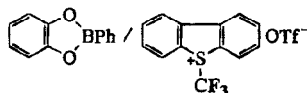
 Me_2SO_4

JACS 109 2426 (1987)

TL 36 5909 (1995) (lactone)

MeI

TL 31 6553 (1990) (chiral)



JOC 59 5692 (1994)

RX (X = halogen or sulfonate ester)

Organomet Chem Syn 1 237 (1971)

JACS 93 2318 (1971); 102 3620 (1980); 104 1735 (1982); 107 1435, 2512, 5570 (lactone) (1985); 108 800, 2451 (lactone) (1986); 109 6858 (1987); 110 3597, 4640 (1988); 112 5875 (1990); 113 2071 (1991); 114 4128, 7007, 8818 (1992); 115 3056 (1993); 117 12159 (1995)

CC 892 (1972) (lactone); 711 (1973); 616 (1980); 904 (1984); 149, 1662 (lactone) (1985); 288 (1986); 992, 1721 (lactone), 1786 (lactone) (1987)

TL 2425 (1973); 21 1137 (1980); 23 5271 (1982); 24 1235, 3213 (1983) (both chiral); 26 397, 5623 (lactone) (1985); 27 1781, 1785, 3247, 3685, 3719, 5335, 5769, 5951 (1986) (all lactones except 3685 and 5951); 28 183, 1623 (lactone), 1685, 1933 (lactone), 2045, 2087, 2849 (chiral), 4629, 5075 (intramolecular), 5161 (lactone), 5205, 5659 (1987); 29 6961 (1988); 30 1579, 2825 (1989); 31 3615, 4027 (intramolecular) (1990); 32 4541, 6885 (intramolecular) (1991); 34 1931, 6557 (intramolecular) (1993); 35 689, 9211 (intramolecular) (1994); 36 5035 (intramolecular), 5909 (lactone), 8299 (intramolecular) (1995)

JCS Perkin I 694 (1977)

Syn 112 (1977); 710 (1980); 305 (1982)

J Polym Sci, Polym Chem Ed 17 3499, 3509 (1979)

RX (X = halogen or sulfonate ester)
(continued)

$\text{Et}_3\text{Al/RX}$

$\text{R}_2\text{C}=\text{CF}_2$ (E = $\text{R}_2\text{C}=\text{CF}$)

$\text{RC}\equiv\text{CCl}$ (R = Cl, Ph, SPh)

ArX , hv

RX (R = aryl, vinylic), Ni catalyst

$p\text{-(NO}_2)_2\text{C}_6\text{H}_4$ (E = $p\text{-C}_6\text{H}_4\text{NO}_2$)

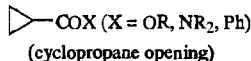
$p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$ (E = $p\text{-C}_6\text{H}_4\text{NO}_2$)



epoxide

epoxide, Et_2AlCl

thiirane



RCHO , R_2CO

JOC 44 2165 (1979); 45 891, 3236 (stereochemistry) (1980); 46 3756 (polymer), 4795 (inter- and intramolecular), 5364 (polymer) (1981); 47 180, 598 (1982); 50 2128 (intramolecular), 2668 (lactone) (1985); 51 4828 (lactone), 5492 (intramolecular) (1986); 52 569, 1309, 2563, 4601 (lactones), 4633 (intramolecular), 4641 (1987); 53 1527, 2440, 4094 (lactone), 4393 (lactone), 6031 (lactone) (1988); 54 1859, 3422 (1989); 56 1176 (lactone), 4929, 7341 (1991); 57 389 (lactone), 2554, 4457, 6067 (lactone) (1992); 58 338 (intramolecular), 3444, 4346 (lactone), 5717, 6857 (lactone); 59 5343 (1994)

Rec Trav Chim 99 141, 311 (1980)

CL 1621 (1981); 81 (1986)

Angew Int 20 207, 574 (1981)

Tetr 37 3981 (1981); 40 2211 (1984)

Can J Chem 60 2007 (1982)

Org Prep Proc Int 15 149 (1983)

Ann 531 (1984)

SL 735 (1992) (inter- and intramolecular); 795 (1993)

JOC 57 2411 (1992)

JOC 57 6643 (1992)

TL 23 2373 (1982)

JACS 106 3551 (1984)

JACS 102 7765 (1980)

JACS 99 4833 (1977)

CL 31 (1986)

CL 173 (1986)

JOC 59 520 (1994)

J Polym Sci, Polym Chem Ed 17 3509 (1979)

JOC 51 4840 (1986)

JACS 112 5875 (1990)

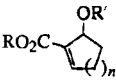
JOC 54 2039 (1989); 56 5951 (1991); 58 7304 (1993)

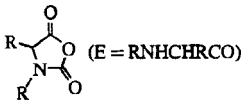
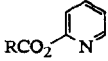
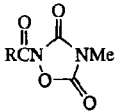
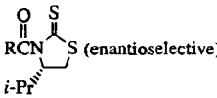


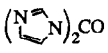
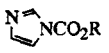
J Polym Sci, Polym Chem Ed 17 3509 (1979)

Ber 114 32 (1981)

JACS 92 3222 (1970); 95 3050 (1973); 101 2501 (1979); 105 1667 (1983) (diastereoselectivity); 106 3252 (1984); 107 1379, 2138 (lactone), 5541 (1985); 108 1019 (1986); 110 3560, 4640 (1988); 111 6234 (1989); 112 4976 (chiral B enolate), 6942 (1990); 113 5337 (1991)

- Org Syn 53 66 (1973); 63 99 (1984)
 Syn 719 (1974); 112 (1977); 297 (1983)
 TL 1745 (1975); 3975 (1980); 23 4285 (lactone),
 5271 (1982); 24 1311 (1983); 27 2489, 3577,
 4601, 4873, 6341, 6345 (1986); 28 655, 1761,
 1925, 3059, 3723 (intramolecular to 2-alken-4-
 olide), 5661, 5921 (1987); 29 2307, 2787
 (intramolecular), 3415 (intramolecular) (1988); 30
 1715, 5115 (1989); 31 3783 (1990); 32 449, 1535,
 5345 (1991); 33 457 (Ti enolate, chiral auxiliary)
 (1992); 34 1737 (chiral B enolate), 6977 (Zr
 enolate) (1993); 35 1325 (1994); 36 3115 (1995)
 (Zr enolate, chiral auxiliary)
 JOC 45 1066, 1726, 3549, 3846 (1980); 50 3022
 (1985) (enones); 51 1402, 5492 (1986); 52 2378
 (lactone), 3541 (lactone) (1987); 53 1922 (1988);
 54 4717 (1989); 56 1176 (lactone), 2853 (1991);
 57 2554, 2888, 3007, 7143 (chiral) (1992); 58
 5717 (1993); 59 2336 (B enolate), 3347 (Ce
 enolate), 6287 (chiral) (1994); 60 758, 1435
 (lactone), 6397, 7778 (Zn enolate) (1995)
 Tetr 37 4087 (1981)
 Acta Chem Scand B 35 273 (1981)
 Helv 64 2592 (1981); 69 1699 (1986)
 CL 57, 929 (1982)
 Angew Int 21 777 (1982) (lactone); 24 874 (1985)
 (diastereoselective)
 Syn Commun 12 225 (1982) (silyl ester)
 CC 305, 878, 1199, 1237 (1986)
 Org Syn Coll Vol 6 598 (1988); 7 190 (1990)
- RCHO, R₂CO (lactone formation)
 RCH(OMe)NHCO₂Me (E = CHRNHCO₂Me)
 (Me₂N⁺=CH₂)X⁻
 RCH=NR' (lactam formation)
 RCH=NCO₂R
 RCH=NOCH₂Ph (lactam formation)
 RCH=NSPh (lactam formation)
 R₂C=NSOAr
 RCH=NSiR₃ (lactam formation)
- See page 1861, Section 8.
 TL 29 231 (1988)
 CC 305 (1986)
 Chem Rev 89 1447 (1989) (review)
 TL 30 1253 (1989)
 CL 369 (1984)
 JOC 51 1929 (1986)
 JOC 57 6387 (1992)
 JOC 48 289 (1983); 50 5120 (1985); 56 5984
 (1991)
 JACS 106 4819 (1984); 110 6879 (1988)
 TL 27 1695 (1986); 28 5369 (1987); 30 4275
 (1989)
 SL 243 (1991)
 JOC 45 3413 (1980); 50 5120 (1985)
 JACS 106 4819 (1984); 108 6054 (1986)
- RCH=NAr (lactam formation)
 JOC 45 3413 (1980); 50 5120 (1985)
 JACS 106 4819 (1984); 108 6054 (1986)

RCH=NAr (lactam formation) (<i>continued</i>)	TL 32 7563 (1991) (Li, Na, Ti, Zn enolates); 33 5737 (1992); 34 1307 (1993) (Li, Ti, Zn enolates); 35 7339 (1994) (chiral); 36 729 (chiral, various enolates), 4213 (chiral) (1995) SL 35 (1992)
RCH=NR (lactam formation)	JOC 56 1933 (1991); 58 2302 (1993) (Zn enolate)
RCH=NR, BF ₃ ·OEt ₂	TL 24 4503 (1983)
RCH=NR, Me ₂ AlCl (lactam formation)	TL 28 3377 (1987)
RCH=NR, 1-(trimethylsilyl)benzotriazole	JOC 60 3405 (1995) (Zn enolate)
RCH=C=NR (lactam formation)	TL 28 4347 (1987)
enal (1,4-addition)	J Polym Sci, Polym Chem Ed 17 3509 (1979)
enone (1,2- or 1,4-addition)	JOC 41 4044 (1976); 47 3464 (1982); 50 3022 (1985) J Polym Sci, Polym Chem Ed 17 3509 (1979) CC 305 (1986) TL 27 3927 (1986) (intramolecular); 35 6357 (1994) (1,4-addition; Li and Ti enolates) Tetr 48 5597 (1992) (1,4-addition; Li and Ti enolates)
enone, MAD (1,4-addition)	TL 28 5723 (1987)
ynone (1,4-addition, intramolecular)	TL 29 3423 (1988)
RCH=CHNO ₂ (1,4-addition)	See page 1511, Section 12.
R ₂ NCH=CRNO ₂ (E = CH=CRNO ₂)	JACS 108 3855 (1986) (chiral, zinc lactone enolate); 111 7921 (1989) (lactones) TL 36 99 (1995) (chiral, zinc lactone enolates)
RCH=CHCO ₂ R(NR ₂) (1,4-addition)	See page 1809, Section 6.
 (<i>n</i> = 1, 2; R' = Ac, SiMe ₃ ; S _N 2' substitution of OR')	TL 28 5521 (1987)
HCO ₂ Me	TL 27 5397 (1986)
RCO ₂ R	Syn 715 (1983); 45 (1985) TL 27 5177 (1986); 28 2017, 2753 (1987); 29 3423 (1988); 30 3857, 6341 (1989); 31 3913 (1990) JOC 57 7143 (1992); 59 2423 (1994)
lactone	TL 4323 (1978); 27 6345 (1986); 28 5661 (1987) JACS 107 1691 (1985); 109 1564 (1987)
RCOCl	TL 2953 (1971); 28 3551 (1987) (lactone); 32 7731 (1991)

	JOC 39 3455 (1974); 46 3756 (polymer), 5364 (polymer) (1981); 51 4813 (1986); 52 4531, 4601 (lactones) (1987); 53 2968 (1988); 57 2566 (1992); 58 6438 (1993); 60 5041 (1995) (lactone)
	Compt Rend 286 401 (1978)
	J Chem Res (S) 44 (1980)
	JACS 102 3620 (1980); 107 5289 (1985); 108 7686 (1986); 109 7488 (1987)
	JCS Perkin I 2885 (1982)
	Syn Commun 13 183 (1983) (silyl ester)
(RCO) ₂ O	JACS 110 6172 (1988)
RCO ₂ CO ₂ R'	JOMC 127 C65 (1977)
	TL 3713 (1978)
	Tetr 37 307 (1981)
	JOC 52 4531 (1987)
 (E = RNHCHR'CO)	TL 32 3115 (1991)
	JOC 52 4531 (1987)
	TL 29 2661 (1988)
	JOC 54 617 (1989)
 (enantioselective)	JOC 53 5983 (1988)
RCOCH	TL 28 4011 (1987)
RCON(Me)OMe	JOC 54 4229 (1989)
RCN	TL 23 1597 (1982)
	JOC 52 4303 (1987)
	Bull Soc Chim Belg 91 871 (1982)
	TL 27 5281 (1986); 28 2837 (1987)
	JACS 109 4717 (1987)
	CC 1228 (1987)
	Bull Soc Chim Belg 91 871 (1982)
	Bull Soc Chim Belg 91 871 (1982)



Bull Soc Chim Belg 91 871 (1982)

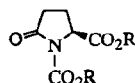


Bull Soc Chim Belg 91 871 (1982)

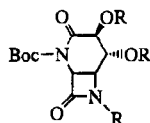


JOC 59 5183 (1994)

TL 36 4547 (1995)



TL 29 4303 (1988); 33 5589 (1992)



SL 139 (1993)



JOC 39 2114 (1974); 46 3151 (1981); 53 4021 (1988); 56 1176 (1991) (lactone); 58 6843 (1993)

J Polym Sci, Polym Chem Ed 17 3509 (1979)

JACS 102 3620 (1980)

JCS Perkin I 2885 (1982)



TL 34 1931 (1993)



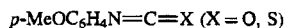
TL 3001 (1971)

JACS 114 8349 (1992)

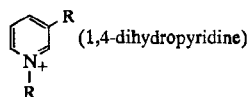


TL 27 1221, 1225, 1229 (1986) (all lactones); 28 1051, 1725 (1987)

JACS 110 5442 (1988); 112 2749 (1990)



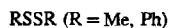
TL 28 3593 (1987)



TL 28 4457 (1987)



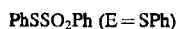
JOC 54 1101 (1989)



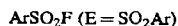
JACS 95 6840 (1973); 98 4887 (1976); 110 879 (1988)

TL 2429 (1973)

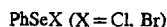
JOC 39 2114 (1974); 57 6067 (1992)



JACS 110 6265 (1988)



JOC 55 1125 (1990)



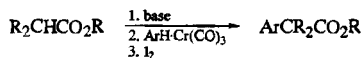
JACS 95 5813 (1973)

JOC 39 2114 (1974); 52 2563 (1987)

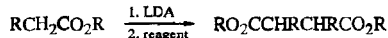
Tetr 34 1049 (1978)

PhSeSePh	JOC 52 2563, 2639 (1987)
TsON(Li)Boc (E = NHBoc)	TL 32 2359 (1991) (Zn enolate)
R ₂ NOPOPh ₂ (E = NR ₂)	TL 36 7701 (1995) (intramolecular)
BocN=NBoc (E = BocNNHBoc)	SL 475 (1993)
2,4,6- <i>i</i> -Pr ₃ C ₆ H ₂ SO ₂ N ₃ (E = N ₃)	JOC 56 7341 (1991) SL 962 (1992)
Ph ₂ MeSiCl	JACS 103 2418 (1981) Syn Commun 13 833 (1983) JOC 53 633 (1988) Org Syn Coll Vol 8 474 (1993) SL 199 (1993)

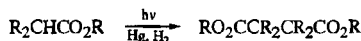
See page 732, Section 6 for halogenation and page 981, Section 7 for hydroxylation.



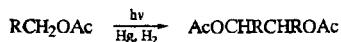
JACS 97 1247 (1975); 99 1675 (1977); 101 217, 3535 (1979)
Pure Appl Chem 53 2379 (1981) (review)
Tetr 37 3957 (1981)
JOMC 226 183 (1982); 240 C5 (1982)
Organomet 2 467 (1983)



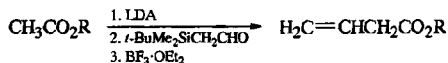
electrolysis	CL 621 (1975)
I ₂	Syn 396 (1975) TL 28 4441 (1987); 36 4409 (1995)
TiCl ₄	CL 1591 (1992)
CuCl ₂	JOC 48 1125 (1983) (intramolecular)
CuBr ₂	JACS 93 4605 (1971) JOC 48 1125 (1983) (intramolecular) TL 33 891 (1992)
(<i>n</i> -C ₄ H ₉ CO ₂) ₂ Cu	JACS 93 4605 (1971) TL 36 4409 (1995)
Cl ₃ CCCl ₃ or BrCMe ₂ CMe ₂ Br	JOC 35 2085 (1970)



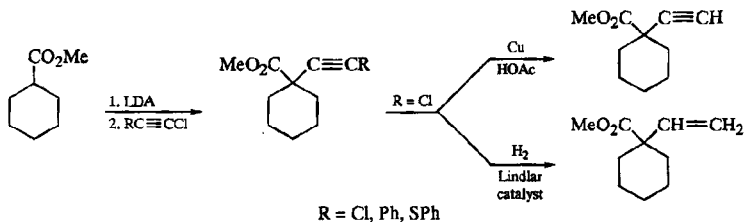
JACS 113 2233 (1991)



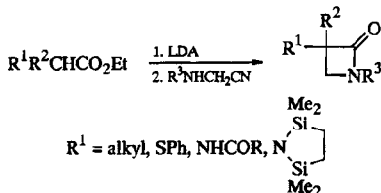
JACS 113 2233 (1991)



JACS 103 6251 (1981)

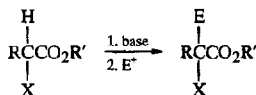


TL 23 2373 (1982)



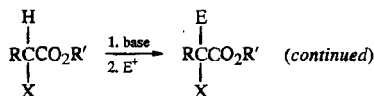
JACS 107 1698 (1985)

JOC 56 1933 (1991)



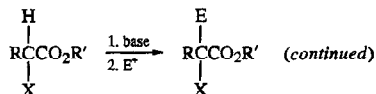
X	E ⁺	
F	R ₂ CO RCHO, R ₂ CO, enone, RCOCl	Syn 322 (1983) TL 31 7043 (1990)
Cl	RX RCHO RCH=NAr	Syn 524 (1975) JACS 110 5533 (1988) Syn 524 (1975) TL 33 7903 (1992) (Ti enolate, forms azetidin-2-one; Li or Zn enolates, forms aziridine)
Cl, Br	RCH=NSiMe ₃ (forms aziridine)	TL 32 121 (1991)
Br	RCHO RCH=NSOAr (forms aziridine)	TL 32 2857 (1991) (chiral B enolate); 33 6735 (1992) (chiral B enolate) JOC 59 1166 (1994) JOC 59 3243 (1994)
I	RCHO	TL 34 7949 (1993) (intramolecular)

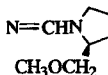
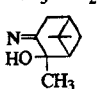
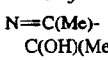
OH	D ₂ O, RX, RCHO, R ₂ CO, epoxide	JOC 42 2948 (1977)
OR	RX	CC 951 (1971) Helv 64 2704 (1981); 65 385 (1982) TL 22 4221 (1981); 28 221 (1987); 35 769 (1994) Angew Int 20 1030 (1981); 21 449 (1982) Ann 1930 (1983) Tetr 40 1313 (1984) (lactone) JOC 51 3746 (1986); 52 3777 (1987); 56 1094 (1991) SL 795 (1993) TL 27 6059 (1986) TL 36 909 (1995)
	ArX (heterocyclic)	
	MeOCHRNHCO ₂ Me (MeO substitution)	TL 1477 (1975); 2835 (1977); 24 5869 (1983); 29 2325 (1988); 35 769 (1994); 36 6965 (1995) JACS 103 4972 (1981); 106 8161 (1984); 112 5583 (1990) Helv 64 2704 (1981) Angew Int 20 1030 (1981) Tetr 40 1313 (1984) (lactone) JOC 50 2095 (1985); 52 3176 (lactone), 3777 (1987); 53 4730 (1988); 54 3487, 4235 (1989) JOC 41 4044 (1976) TL 4323, 4327 (1978) JOC 52 3777 (1987)
	RCHO, R ₂ CO	
	enone (1,2- or 1,4-addition)	
	lactone	
	Ac ₂ O, AcCl, RCO ₂ R, H ₂ C=CHCO ₂ R (1,4-addition), CO ₂ , (CN) ₂	
OSiR ₃	RCHO	JOC 58 5301 (1993)
	RCH=NSiMe ₃ (lactam formation)	JOC 56 1681 (1991) J Med Chem 35 4230 (1992)
	RCH=CHCO ₂ R (1,4-addition)	JOC 58 5301 (1993)
SR	RX	Syn Commun 3 265 (1973) BCSJ 50 242 (1977) (lactone) JACS 100 7424 (1978) (intramolecular) TL 24 3391 (1983) JOC 57 6067 (1992) TL 34 5043 (1993); 35 8525 (1994) (lactone)
	epoxide	
	RCHO	TL 24 523 (1983) JOC 48 2705 (1983); 52 4631 (1987) (lactone) CC 717 (1985) JOC 41 4044 (1976) JACS 106 4819 (1984)
	enone (1,2- or 1,4-addition)	
	PhCH=NSiMe ₃ (lactam formation)	



$\underline{\text{X}}$	$\underline{\text{E}}^+$	
SO ₂ Ph	RX	TL 33 3039 (1992) JOC 59 8081 (1994) (lactone) JOC 59 8081 (1994) (lactone)
	H ₂ C=CHCO ₂ Et, HC≡CCO ₂ Et (both 1,4-addition)	
SePh	RX	JACS 95 6137 (1973) TL 27 3297 (1986)
	RCHO	JACS 103 4114 (1981)
SiMe ₃	RX	JOC 54 1408 (1989)
NO ₂	RX	BCSJ 43 2277 (1970); 46 337 (1973) JOC 58 779 (1993)
NMe ₂	RCHO	TL 1477 (1975)
NR ₂	D ⁺ , RX, RCHO, R ₂ CO, C ₆ H ₅ ·Cr(CO) ₃ (E = Ph), PhSSPh	JACS 105 5390 (1983)
	RX	Helv 64 2704 (1981) CC 1329 (1987) TL 29 6079 (1988) JACS 112 808 (1990); 116 10809 (1994)
	RCHO	TL 32 5521 (1991) (B enolate)
	RCHO, R ₂ CO	CC 1329 (1987)
	RCH=NR (R ₂ AlCl, lactam formation)	JACS 113 5742 (1991) JOC 57 3906 (1992)
	RCH=NR (Li, Ti or Zn enolate; lactam formation)	SL 59 (1993)
	RCH=NR' (R' = Me, SiMe ₃ , Zn enolate; lactam formation)	TL 30 765 (1989)
	RCH=NR (EtZnCl or ZnCl ₂ , lactam formation)	Rec Trav Chim 106 516 (1987) JOC 56 5147 (1991); 57 3906 (1992)
	pyridinium salt	TL 31 747 (1990)
N(SiMe ₃) ₂	RX	Angew Int 7 809 (1968) Z Chem 10 392 (1970) Angew Int 7 809 (1968); 21 210 (1982) Z Chem 10 393 (1970) JOC 44 3967 (1979) (R' = SiMe ₃) TL 28 2849 (1987)
	RCHO, R ₂ CO	TL 29 2467 (1988) JOC 56 5147 (1991)
	RCH=NR (ZnCl ₂ , lactam formation)	
$\begin{array}{c} \text{Me}_2 \\ \diagup \text{Si} \\ \diagdown \text{Si} \\ \text{N} \end{array}$	RX, RCHO	TL 22 1787 (1981)
	RCH=NR (lactam formation)	TL 28 5369 (1987); 29 2467 (1988) (Zn enolate); 31 4289 (1990) Rec Trav Chim 106 516 (1987) (Zn enolate) JACS 113 5742 (1991) (Al enolate)

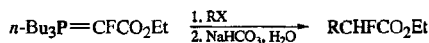
		JOC 56 5147 (Zn enolate), 5868 (Li, Zn enolate) (1991)
NHCHO	RX	Angew Int 20 971 (1981)
NHCOR	RX epoxide (lactone formation)	JOC 60 1233 (1995) JOC 58 6966 (1993)
NRCHO	RX	JACS 116 10809 (1994)
NRCOR	D ₂ O RX	TL 2205 (1976) TL 2205 (1976); 28 2243 (1987) Pol J Chem 53 2397 (1979) JACS 109 4649, 6537 (1987); 112 770 (1990); 116 10809 (1994)
	RCHO	CC 1738 (1987) TL 29 3109 (1988)
	RCHO, R ₂ CO, RCOCl	JOC 46 2809 (1981)
	RCOCl, (RCO) ₂ O	CC 753 (1978)
	RCOCl	CC 1283 (1987)
	PhSeCl	TL 29 4305 (1988)
NHCO ₂ R	RCHO, R ₂ CO	JOC 44 3967 (1979) SL 945 (1995) (Ti enolate)
NRCO ₂ R	RX	TL 29 6079 (1988) (chiral); 33 1573, 1577 (1992) (both chiral) JOC 58 860 (1993) JACS 116 10809 (1994) (chiral)
	RCHO	JOC 52 2881, 4804 (1987) TL 33 1573 (1992)
N=C:	RX RCH=CHCO ₂ R (1,4-addition)	Angew Int 10 331 (1971) Ann 1571 (1973)
N=CHR	chiral RCO ₂ H RX	TL 21 2521 (1980) JOC 41 3491 (1976); 55 3147 (1990) TL 1455 (1977); 23 4255, 4259 (1982); 27 4435 (1986); 33 1565 (1992) BCSJ 55 961 (1982) (enantioselective) JACS 110 8520 (1988) Syn 789 (1983)
	PhCH ₂ SeCH ₂ Br	JOC 51 2981 (1986)
	Ph ₃ BiCO ₃ (E = Ph)	TL 30 3909, 3913 (1989)
	H ₂ CO	Syn 445 (1981)
	RCHO	TL 34 677 (1993) (Ti enolate)
	RCH=CHCOR (1,4-addition)	JOC 41 3491 (1976); 55 4411 (1990)
	RCH=CHCO ₂ R (1,4-addition)	JOC 41 3491 (1976); 55 4411 (1990) TL 1455 (1977)
	RCH=CHCN (1,4-addition)	TL 1455 (1977)
N=CHNMe ₂	RX, epoxide (lactone), ArCH=C(CO ₂ R) ₂ *, ArCH=CHNO ₂ *, H ₂ C=CHCO ₂ R* (*1,4-addition)	JOC 42 2639 (1977)



<u>X</u>	<u>E</u> ⁺	
	$\text{PhCH}_2\text{SeCH}_2\text{Br}$	JOC 51 2981 (1986)
	RX	Ann 1668 (1983) (chiral)
	RX	TL 24 3721 (1983) (chiral); 30 6011 (1989)
	RCHO	CL 279 (1981) (chiral)
$\text{N}=\text{CR}_2$	RX	CC 136 (1976) TL 23 2863, 4255 (1982); 27 3839 (1986) (chiral); 28 3801 (1987); 29 2441 (1988); 34 1917, 8535 (1993); 36 5823 (1995) JACS 110 8520 (1988); 111 2353 (1989) (chiral catalysis) JOC 53 1947 (1988) (chiral); 57 757 (1992); 58 954, 957, 1613 (1993); 59 7752 (1994); 60 1891, 2292, 2968 (1995) SL 247 (1994) JOC 51 2981 (1986) TL 30 3909 (1989) TL 36 7697 (1995) TL 27 23, 4573 (1986); 29 4981 (1988) (intramolecular) SL 226 (1995) TL 31 3133 (1990)
	$\text{PhCH}_2\text{SeCH}_2\text{Br}$	
	Ph_3BiCO_3 (E = Ph)	
	allylic halide, cat $\text{Pd}(\text{PPh}_3)_4$	
	$\text{H}_2\text{C}=\text{CRCH}_2\text{O}_2\text{CX}$ (X = Me, OEt), cat PdL_2 (E = $\text{H}_2\text{C}=\text{CRCH}_2$)	
	chiral π -allylpalladium complex (E = allylic)	
	$\text{HC}\equiv\text{CCO}_2\text{R}$ (E = $\text{CH}=\text{CHCO}_2\text{R}$)	TL 36 5823 (1995)
	RCHO	CL 145 (1982) TL 29 2067 (1988) JOC 59 3240 (1994) (Ti enolate) JOC 53 1947 (1988); 56 2875 (1991); 58 4221 (1993) (chiral) JOC 53 1947 (1988)
	$\text{RCH}=\text{CHCO}_2\text{R}$ (1,4-addition)	
	$\text{RCH}=\text{C}(\text{CO}_2\text{R})_2$ (1,4-addition)	
$\text{N}=\text{C}=\text{O}$	$\text{RCH}=\text{NR}$, $\text{BF}_3\cdot\text{OEt}_2$	TL 24 4503 (1983)
$\text{N}=\text{C}=\text{S}$	$\text{RCH}=\text{NR}$, $\text{BF}_3\cdot\text{OEt}_2$	TL 24 4503 (1983) JACS 105 5946 (1983)
$\text{N}=\text{C}(\text{SR})_2$	RX	Angew Int 14 426 (1975) JOC 60 7934 (1995) (chiral) JOC 60 6700 (1995) JOC 60 6700 (1995)
	enone (1,4-addition)	
	$\text{RCH}=\text{CHCO}_2\text{R}$ (1,4-addition)	

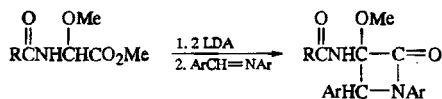
N₃ RCHO TL 34 7953 (1993); 35 8891 (1994)
 (both intramolecular)

SiR₃ RX JOC 57 2554 (1992)

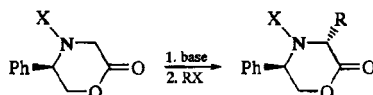


TL 30 3641 (1989)

JOC 55 2311 (1990)

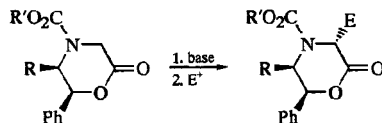


Syn 407 (1982)



X = CH₂Ph, Boc

JOC 54 3916 (1989)



R E⁺
H RX

TL 29 6079 (1988)

JOC 54 2251, 3916 (1989)

Ph RX TL 29 6075 (1988); 33 7725 (1992); 35 9371 (1994); 36
 825 (1995)

JACS 113 6976, 9276 (1991)

SL 249 (1992)

JOC 57 6519 (1992)

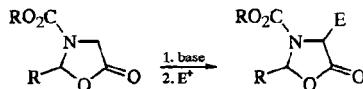
RCHO TL 31 827 (1990) (B enolate)

JACS 113 6976 (1991) (B enolate)

JOC 57 6519 (1992) (B enolate)

TL 36 825 (1995)

H₂C=C(CO₂R)₂
 (1,4-addition)



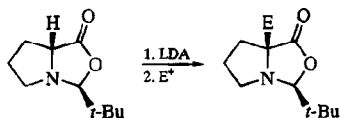
E⁺

RX JOC 58 14 (1993); 60 5719 (1995)

epoxide, BF₃·OEt₂ JOC 59 7671 (1994)

epoxide, Et₂AlCl TL 35 8977 (1994)

JACS 117 11113 (1995)

 E^+

RX

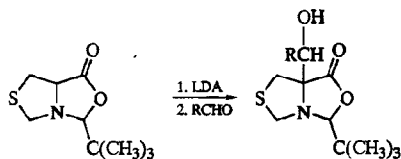
JACS 105 5390 (1983)

Org Syn 72 62 (1993)

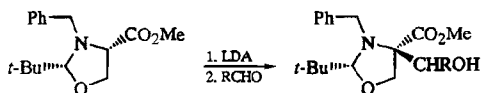
JOC 60 115 (1995)

$(H_2C=NMMe_2)Cl$, $RCHO$, R_2CO , RCO_2R ,
 $(RCO)_2O$, $ClCO_2R$, $RSSR$, $RCH=CHNO_2$
 (1,4-addition)

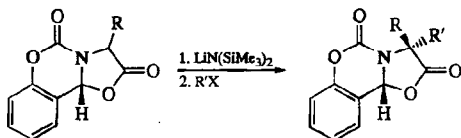
JACS 105 5390 (1983)



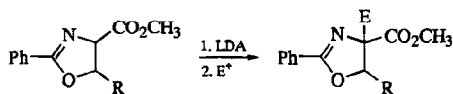
TL 24 3315 (1983)



JACS 114 10677 (1992)



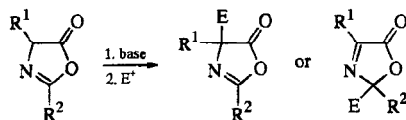
JOC 55 5437 (1990)

 $E^+ = D^+$, RX , $RCHO$, R_2CO

TL 24 3311 (1983); 34 6969 (1993)

JOC 52 3326 (1987)

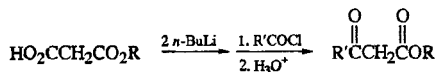
JACS 115 5302 (1993)



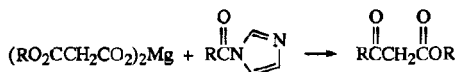
$\text{E}^+ = \text{RX}, \text{RCOCl}, \text{Michael acceptors}$

Ber 102 883 (1969); 113 3706 (1980)

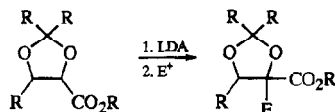
Angew Int 10 653 (1971)



See page 1528, Section 22.

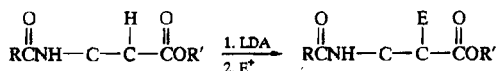


See page 1528, Section 22, for this and related reactions.

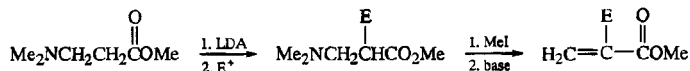


$\text{E}^+ = \text{RX}, \text{R}_2\text{CO}$

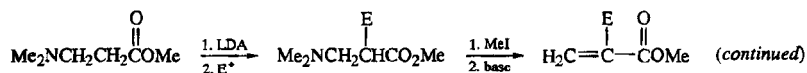
Ber 116 3413 (1983)



R	E^+	
H	RX	Angew Int 20 971 (1981)
Ph	RX	TL 24 2733 (1983) (lactone); 28 3103 (1987)
	RCHO	JACS 108 4943 (1986) (lactone)
		TL 28 3103 (1987); 35 3901 (1994)
OR	RX	TL 24 2733 (1983); 30 4349 (1989) (both lactones)
	RCHO	TL 35 3901 (1994)
	R_2CO	JACS 105 1659 (1983) (lactone)



E^+	
RX	TL 3423 (1978)
	JOC 46 4536 (1981)
	Syn Commun 11 591 (1981)

 E^+

RCHO

CC 1112 (1983)

JOC 49 3784 (1984); 50 157 (1985); 52 5452 (1987);

60 143 (Al enolate), 6515 (1995)

CC 1660 (1993) (B enolate)

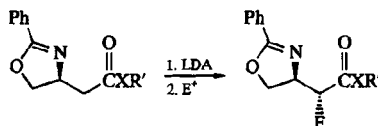
RCH=NR (lactam formation)

JOC 59 7994 (1994)

ArCH=NSiMe₃ (lactam formation)

JACS 106 4819 (1984)

JOC 59 7994 (1994)

 X E^+

O

RX

TL 24 2733 (1983)

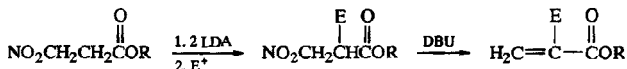
S

RX

JACS 107 1435 (1985); 108 4943 (1986)

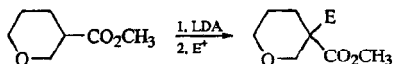
RCHO

JOC 51 3742 (1986)

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{enone (1,4-addition)}$

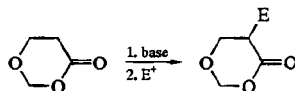
Ber 115 1705 (1982)

Helv 65 385 (1982)

 $\text{E}^+ = \text{MeI}, \text{RCHO}, \text{I}_2, \text{O}_2, (\text{RS})_2, \text{PhSeBr}$

Can J Chem 64 1781, 1788 (1986)

TL 36 2641 (1995)

 E^+

RX

Helv 71 1143 (1988)

Ber 124 1837 (1991)

Chimia 47 19 (1993)

BrCH=CHX (X = CO₂R, SO₂Ar)

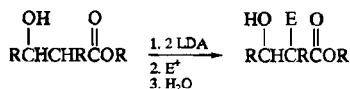
JOC 59 7921 (1994)

RCHO

Ber 123 2413 (1990)

RO₂CN=NCO₂R

TL 29 6765 (1988)

E⁺D₂O

JOC 60 3529 (1995)

RX

TL 2429 (1973); 22 425 (1981); 23 3055, 4991 (1982); 27 5281 (1986); 28 35, 3189, 5033 (3-hydroxy-4-alkanolide) (1987); 30 2707 (1989); 32 2395 (1991); 33 6763, 6803 (1992); 35 4389 (1994) (3-hydroxy-4-alkanolide)

Helv 62 2825, 2829 (1979); 63 197, 1383 (1980); 65 293, 344 (1982)

JOC 46 4319 (1981); 48 1114 (1983); 49 2168 (1984) (3-hydroxy-4-alkanolide); 52 1780 (1987); 57 4793 (1992); 58 7768 (1993); 59 1166, 7201 (3-hydroxy-4-alkanolide) (1994); 60 1120, 3916 (1995)

Ber 114 2786, 2802 (1981)

Ann 939, 2114 (1983)

Org Syn 63 109 (1984)

JACS 107 5292 (1985); 108 2105 (1986); 111 6247 (1989); 112 5583 (1990); 116 1753 (1994); 117 5757 (1995)

CC 1368 (1987)

SL 283 (1991)

RCHO (ZnCl₂)

JOC 46 4319 (1981); 49 2168 (1984) (3-hydroxy-4-alkanolide)

R₂CO

Helv 63 197 (1980)

RCH=CRNO₂ (1,4-addition)

Helv 63 2005 (1980)

RCH=NAr (lactam formation)

TL 25 3779 (1984); 26 3903 (1985); 28 4489 (1987); 31 3267, 7631 (1990)

CC 1433 (1985)

JACS 109 1129 (1987)

RCH=NSiMe₃ (lactam formation)

JACS 106 4819 (1984)

TL 26 937, 5493 (1985)

CL 1927 (1984); 651 (1985)

RCH=NCO₂R

TL 28 69, 83 (1987); 30 1253 (1989); 31 7631 (1990)

CF₃CH=CHCO₂Et (1,4-addition)

JOC 60 4363 (1995)

t-BuO₂CN=NCO₂-*t*-Bu

TL 29 6765 (1988)

MeZnBr / *t*-BuO₂CN=NCO₂-*t*-Bu

SL 475 (1993)

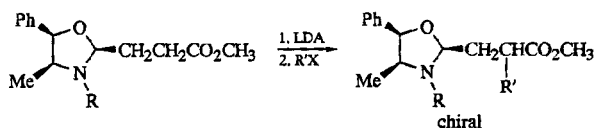
(MeS)₂

TL 2429 (1973)

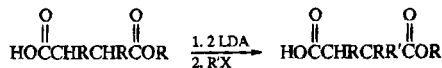
I₂ (epoxide formed)

TL 4575 (1977)

Helv 63 197 (1980)

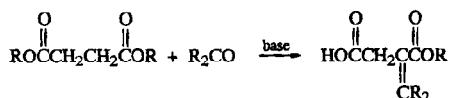


Syn Commun 17 241 (1987)

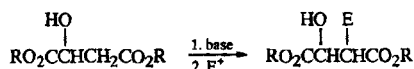


SL 137 (1993)

TL 35 5501 (1994)



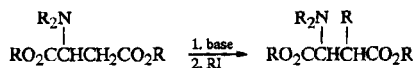
See page 317, Section 3.

 $\text{E}^+ = \text{RX}, \text{R}_2\text{CO}, \text{I}_2$ (epoxide), $\text{C}=\text{C}-\text{NO}_2$ (1,4-addition)

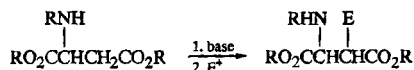
Helv 63 197, 2005 (1980); 65 344, 620 (1982)

Ann 2114 (1983); 407 (1984)

Org Syn Coll Vol 7 153 (1990)



JOC 54 3164 (1989); 55 3068, 5017 (1990)

 E^+

RX

JOC 54 3164 (1989); 55 3068 (intramolecular), 5017 (1990)

 $\text{MoO}_5, \text{py-HMPA}$ ($\text{E} = \text{OH}$)

TL 33 4637 (1992)

JOC 59 7643 (1994)

 $\text{PhSO}_2\text{N} \begin{array}{c} \diagup \text{O} \diagdown \end{array} \text{CHPh}$ ($\text{E} = \text{OH}$)

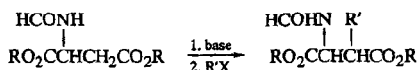
JOC 59 7643 (1994)

 ArSO_2N_3 ($\text{E} = \text{N}_3$)

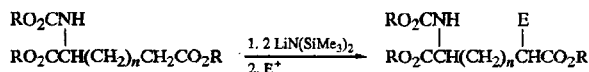
JOC 59 7643 (1994)

 $\text{RO}_2\text{CN}=\text{NCO}_2\text{R}$ ($\text{E} = \text{RO}_2\text{CNNHCO}_2\text{R}$)

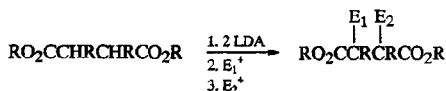
JOC 59 7643 (1994)




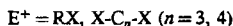
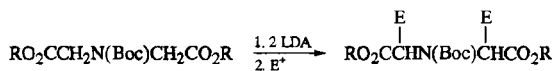
Angew Int 20 971 (1981)



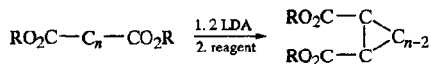
\underline{n}	$\underline{\text{E}}^+$	
0	RX, RCHO	JCS Perkin I 833 (1989) Tetr 45 6309, 6319 (1989) TL 35 8859 (1994)
1	RX, RCHO	TL 35 6335 (1994)



$\underline{\text{E}}_1^+$	$\underline{\text{E}}_2^+$	
D ₂ O	D ₂ O	JACS 100 7753 (1978)
Me ₃ SiCl	Me ₃ SiCl	Syn Commun 11 687 (1981) (O silylation)
RX	H	JACS 111 2302 (1989)
RX	RX or R'X	TL 73 (1979); 23 3683 (1982) Syn Commun 11 687 (1981) CL 687 (1982) JACS 112 9645 (1990)
RCHO, R ₂ CO	HCl	CL 687 (1982)
RCHO	RCHO	TL 73 (1979) JOC 47 4731 (1982)
X—C _n —X (n = 1–5)		TL 1815 (1979); 27 5951 (1986); 28 589 (1987) Syn 389 (1980) Syn Commun 14 227 (1984) JOC 49 1412 (1984); 50 5727 (1985) JACS 107 3343 (1985) (chiral) Org Syn Coll Vol 8 141 (1993)
		TL 28 351 (1987)
BrCH ₂ CH ₂ COCH ₃		JOC 50 5727 (1985)
Br—C _n —CO ₂ Et (n = 2, 3)		TL 22 1755 (1981) JOC 47 4731 (1982); 51 5450 (1986) Syn Commun 14 227 (1984)
RCH=C(CH ₂ Br)CO ₂ Me		TL 25 669 (1984); 27 5951 (1986)
RC≡CCO ₂ Ph		JACS 109 7534 (1987)
o-BrCH ₂ ArCO ₂ Me		TL 23 1031 (1982) JOC 49 2785 (1984)
o-EtO ₂ CC ₆ H ₄ CO ₂ Et		TL 73 (1979); 23 1031 (1982)
H ₂ C=CHCO ₂ Ar		TL 27 5951 (1986); 28 5241 (1987)
TsOCH=CHCOC(CH ₃) ₃		TL 27 5951 (1986)



SL 1023 (1994)

Reagentn I_2

2 (alkene), 5

Syn Commun 14 227 (1984)

TL 28 1831 (1987)

 $\text{Cu}(\text{OTf})_2$

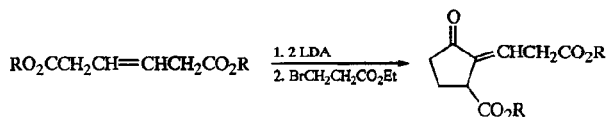
3, 6

Chem Pharm Bull 28 262 (1980)

 CuCl_2 or CuBr_2

3-6

JOC 48 1125 (1983); 52 3462 (1987)



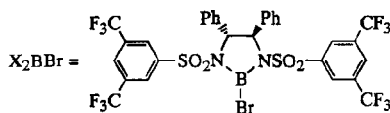
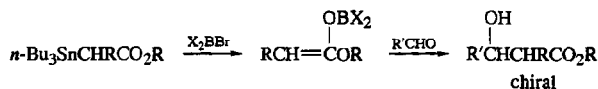
TL 25 671 (1984)



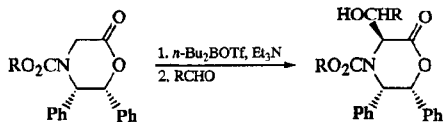
JOC 54 1500 (1989)



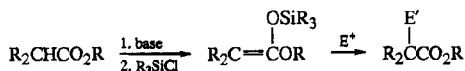
JOC 57 2511 (1992)



TL 31 3715 (1990)



TL 31 827 (1990)



Synthesis of ketene silyl acetals

JACS 98 2868 (1976)

JOC 55 157 (1990); 56 650 (1991)

SL 213 (1994)

Electrophiles (E^+)

 chiral binaphthol- SnCl_4 ($E' = \text{H}$) (enantioselective) JACS 116 11179 (1994)

MeOTf, MABR JACS 114 4422 (1992)

 1°RI , AgO_2CCF_3 TL 33 1855 (1992)

 R_2CCl , ZnCl_2 TL 1455 (1978)
Tetr 37 319 (1981)
Ber 116 3708 (1983)

 ArX ($\text{X} = \text{Br}$, OTf), cat'($\eta^3\text{-C}_4\text{H}_7\text{PdOAc}$) $_2$, cat dppf, LiOAc or TiOAc ($E' = \text{Ar}$) JOC 56 261 (1991)

 $\text{NO}_2\text{-Ar-H}$, $[(\text{Et}_2\text{N})_3\text{S}]\text{Me}_3\text{SiF}_2/\text{Br}_2$ or DDQ JACS 107 5473 (1985)
($E' = 4\text{-NO}_2\text{-Ar}$)

 $\text{ArCH}_2\text{OCOCl}$, AgOTf ($E' = \text{ArCH}_2$) TL 33 951 (1992)

 ArCR_2OAc , ZnCl_2 Ber 116 3708 (1983)

 $(\text{Ar}_2\text{CH})\text{OTf}$ TL 34 3393 (1993)

 $\text{R}_2\text{C}=\text{CHCH}_2\text{X}$ ($\text{X} = \text{Cl}$, Br), high pressure TL 25 1075 (1984)

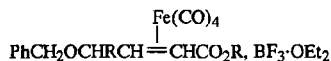
 $\text{RCH}=\text{CHCH}_2\text{OH}$, LiClO_4 ($E' = \text{RCH}=\text{CHCH}_2$) TL 33 4735 (1992)
JOC 57 2986, 6783 (1992)

 $\text{RCH}=\text{CHCH}_2\text{OAc}$, LiClO_4 ($E' = \text{RCH}=\text{CHCH}_2$) JOC 57 2986, 6783 (1992)

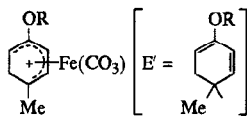
 $\text{R}_2\text{C}=\text{CRCH}_2\text{OAc}$, cat ($\eta^3\text{-C}_4\text{H}_7\text{PdOAc}$) $_2$, cat diphosphine JOC 56 3924 (1991)

 $\text{H}_2\text{C}=\text{CHCH}_2\text{OCO}_2\text{Me}$, cat $\text{Pd}_2(\text{DBA})_3\cdot\text{HCCl}_3$, cat dppe ($E' = \text{H}_2\text{C}=\text{CHCH}_2$) TL 25 4783 (1984)

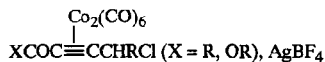
 $\text{PhSCHRCH}(\text{OAc})\text{CH}=\text{CHR}$, cat Me_3SiOTf TL 32 4311 (1991)
($E' = \text{PhSCHRCHCH}=\text{CHR}$)



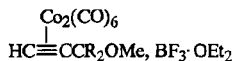
TL 34 4497 (1993)



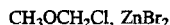
TL 29 869 (1988)



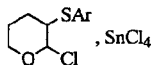
JOC 60 7496 (1996)



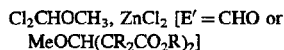
TL 36 1193 (1995)



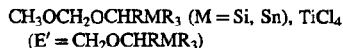
CC 305 (1986)



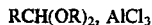
TL 34 3047 (1993)



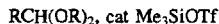
Syn 723 (1982)



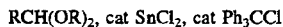
JACS 112 7438 (1990)



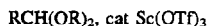
TL 34 7623 (1993)



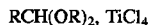
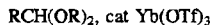
JOC 58 579 (1993)



CL 491 (1987)



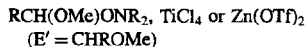
SL 472 (1993)

TL 26 2535 (1985) (chiral); 34 7623 (1993)
JOC 59 1166 (1994)

Syn 371 (1993)



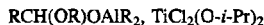
CL 1759 (1984)



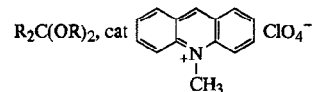
JACS 107 2569 (1985)



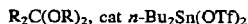
JOC 57 1 (1992)



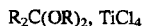
TL 34 5729 (1993)



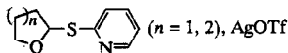
TL 32 2405 (1991)



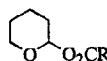
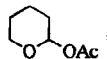
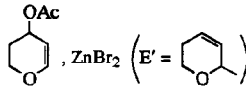

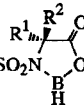


JACS 112 901 (1990)

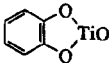


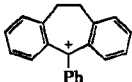
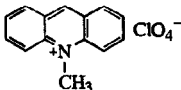



TL 28 1313 (1987) (intramolecular)

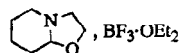


JACS 107 4289 (1985)

- 
 O_2CR , Me_3SiOTf TL 28 1035 (1987) (intramolecular)
- 
 OAc , ZnBr_2 TL 35 9371 (1994)
- 
 OAc , ZnBr_2 ($\text{E}' = \text{cyclohexene}$) JOC 57 3261 (1992)
- $\text{F}_2\text{CHCH}(\text{OH})\text{OEt}$, ZnX_2 ($\text{X} = \text{Cl}, \text{I}$)
 $(\text{E}' = \text{F}_2\text{CHCHOH})$ JOC 58 2302 (1993)
- RCHO or R_2CO JOC 53 554 (1988); 58 988 (1993); 59 5136 (1994)
 (enantioselective)
 JACS 114 7922 (1992); 116 7026 (1994)
- RCHO or R_2CO , high pressure TL 25 1075 (1984)
- RCHO , cat LiClO_4 TL 34 1119 (1993)
- RCHO , MgBr_2 JOC 52 888 (1987); 57 456 (1992)
 (diastereoselection)
 TL 31 6733 (1990)
 SL 285 (1991)
- RCHO , cat TsN - JOC 56 2276 (1991)
 TL 33 1729 (1992)
- RCHO , ArSO_2N - (enantioselective)
 JOC 56 2276 (1991)
 JACS 113 9365 (1991) (catalytic)
 TL 33 4927 (1992) (catalytic); 35 5239, 5243
 (catalyst on polymer) (1994)
- RCHO , cat 2,5-(*i*-PrO) $_2\text{C}_6\text{H}_3\text{CO}_2\text{CH}(\text{CO}_2\text{H})$ - SL 439 (1991)
 (enantioselective)
- RCHO , $\text{BF}_3 \cdot \text{OEt}_2$ JACS 105 1667 (1983)
 JOC 51 3027 (1986) (diastereoselection); 54 83
 (1989); 57 456 (1992) (diastereoselection)
 TL 28 5615 (1987); 31 1443, 6733 (1990)
- RCHO , Ph - Ph (enantioselective) TL 27 4721 (1986)
- RCHO , cat $(\text{C}_6\text{F}_5)_3\text{B}$ SL 577 (1993)
- RCHO , EtAlCl_2 JOC 54 83 (1989)
 TL 31 3909 (1990)
- RCHO , cat Me_3SiCl , cat SnCl_2 CL 463 (1987)
- RCHO , cat SnCl_2 , cat Ph_3CCl CL 491 (1987)

RCHO, Sn(OTf) ₂ , <i>n</i> -Bu ₃ SnF, chiral diamine (enantioselective)	CL 1319 (1989)
RCHO, SnCl ₄	TL 25 5973 (1984); 31 3909; 6733 (1990) JOC 51 3027 (1986); 57 456 (1992) (both diastereoselection)
RCHO, cat BiCl ₃	TL 29 4719 (1988)
RCHO, cat Sc(OTf) ₃	SL 472 (1993)
RCHO, TiCl ₄	TL 4029 (1979); 25 4655 (1984); 30 5163 (1989); 31 217, 6733 (1990); 33 4921 (1992) (diastereoselectivity) CL 531 (1983) JACS 106 5304 (1984); 107 5812 (1985) (enantioselective); 116 8116 (1994) Angew Int 24 874 (1985) (diastereoselective) JOC 51 5032 (1986); 52 2754 (1987) (enantioselective); 53 4015 (1988) (diastereoselective); 54 83 (1989); 57 441, 456 (both diastereoselective), 2034 (1992) Helv 69 1699 (1986) (diastereoselective) SL 285 (1991)
PhCHO, TiCl ₄ (E' = PhCHCl)	TL 29 1275 (1988)
RCHO, TiCl ₄ , R ₃ P	TL 27 1735 (1986)
RCHO, (<i>i</i> -PrO) ₂ TiCl ₂	JOC 59 4370 (1994)
RCHO, (<i>i</i> -PrO) ₃ TiCl	TL 33 4921 (1992)
RCHO, chiral Ti catalyst	JACS 116 8837 (1994)
RCHO, cat 	CL 1909 (1989)
RCHO, cat Cp ₂ M(OTf) ₂ (M = Ti, Zr)	TL 33 6423 (1992)
RCHO, cat Zr(OTf) ₂ (tmtaa) (tmtaa = dibenzotetramethyltetraazannulene)	SL 857 (1994)
RCHO, cat [Cp ₂ Zr(O- <i>i</i> -Bu)(THF)]BPh ₄	JOC 58 3591 (1993)
RCHO, cat CpFe(CO) ₂ X (X = Cl, Br, I)	TL 30 6435 (1989)
RCHO, cat CpFe(dppe)(MeCOMe)X (X = BF ₄ , PF ₆)	CC 1634 (1992)
RCHO, Rh catalyst	TL 28 793 (1987)
RCHO, ZnX ₂ (X = halogen)	TL 29 1803, 5291 (1988)
RCHO, cat ZnX ₂ (X = Cl, Br, I)	JOC 53 554 (1988)
RCHO, cat HgI ₂	JOC 58 2324 (1993)
RCHO, cat Sm(OR) ₂	JOC 58 4771 (1993)
RCHO; cat SmCl ₃ , CeCl ₃ , LaCl ₃ or Eu(fod) ₃	TL 28 5513 (1987); 33 1465 (1992)

RCHO, cat M(dppm) ₃ (M = Pr, Ho)	Tetr Asym 2 993 (1991)
RCHO, cat M(fod) ₃ (M = Pr, Ho, Yb)	TL 33 1465 (1992)
RCHO, cat Eu(fod) ₃	TL 33 1465 (1992)
RCHO, cat Eu(dppm) ₃	JOC 56 5456 (1991) Tetr Asym 2 993 (1991) CL 29 (1992)
RCHO, cat M(OTf) ₃ (M = Eu, Gd, Ho, Yb)	Syn 371 (1993) -
RCHO, cat YbX ₃ (X = Cl, OTf)	JOC 58 4771 (1993)
RCHO, cat [(Me ₃ Si) ₂ C ₂ H ₃] ₂ YbCl, Me ₃ SiCl	JOC 55 6235 (1990)
RCHO, cat  X ⁻ (X = OTf, ClO ₄)	TL 35 4327 (1994)
RCHO, various catalysts	TL 35 4323 (1994)
RCHO or R ₂ CO, cat  ClO ₄ ⁻	TL 32 2405 (1991)
R ₂ CO, hv	JOC 58 5405 (1993)
R ₂ CO, AlCl ₃ or FeCl ₃	Syn Commun 13 449 (1983)
R ₂ CO, SnCl ₄	SL 275 (1994)
R ₂ CO, TiCl ₄	Syn Commun 13 449 (1983) SL 397 (1990)
R ₂ CO, cat Cp ₂ M(OTf) ₂ (M = Ti, Zr)	TL 33 6423 (1992)
PhSCH ₂ Cl, ZnBr ₂	TL 993 (1979) CC 305 (1986)
PhSCHClR, TiCl ₄ or ZnBr ₂	TL 2179 (1979); 23 2399 (1982) CC 1472 (1987)
PhSCH ₂ CH ₂ Cl, ZnBr ₂	TL 24 1315 (1983)
	CC 305 (1986)
 , cat CF ₃ SO ₃ H (E' = CH ₂ NHR)	TL 24 913 (1983)
MeLi /  (E' = CHNR ₂)	TL 31 3999 (1990)
R ₂ NCH ₂ OR, ZnCl ₂ (E' = CH ₂ NR ₂)	BCSJ 56 645 (1983)
(Me ₃ Si) ₂ NCH ₂ OCH ₃ , cat Me ₃ SiOTf [E' = CH ₂ N(SiMe ₃) ₂]	CC 883 (1984)



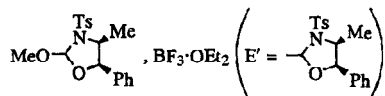
JOC 60 2922 (1995)

$\text{Me}_2\text{NCH(OMe)}_2$, ZnCl_2 (3-dimethylamino-2,4-dialkylpentanedioate diesters)

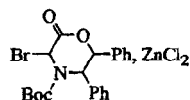
Syn 787 (1983)

$\text{MeOCHRNRCO}_2\text{R}$, cat Me_3SiOTf

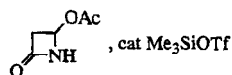
SL 619, 621 (1990)



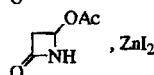
TL 31 2779 (1990)



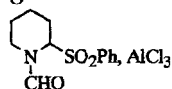
JACS 110 1547 (1988)



TL 28 507 (1987)



CL 1343 (1985)



SL 48 (1990)



SL 87 (1991)

RCHO , $\text{R}'\text{NH}_2$, cat Yb(OTf)_3 , MgSO_4 or molecular sieves ($\text{E} = \text{CHRNHR}'$)

TL 36 5773 (1995)

$\text{RCH}=\text{NR}'$, montmorillonite clay ($\text{E}' = \text{CHRNHR}'$)

SL 141 (1993)

$\text{RCH}=\text{NR}'$, montmorillonite clay, K_{10} or $p\text{-TsOH}$ ($\text{E}' = \text{CHRNHR}'$)

TL 34 2123 (1993)

$\text{RCH}=\text{NR}'$, KF, 18-crown-6 (β -lactam)

TL 34 2123 (1993)

$\text{RCH}=\text{NR}'$, chiral binaphthol boronate ($\text{E}' = \text{CHRNHR}'$)

JACS 115 1151 (1993); 116 10520 (1994)
SL 239 (1993); 41 (1995)

$\text{RCH}=\text{NR}'$, $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{E}' = \text{CHRNHR}'$)

TL 35 3737 (1994)

$\text{RCH}=\text{NR}'$, cat $(\text{C}_6\text{F}_5)_3\text{B}$ ($\text{E}' = \text{CHRNHR}'$)

SL 963 (1994)

$\text{RCH}=\text{NR}'$, cat Me_3SiOTf ($\text{E}' = \text{CHRNHR}'$)

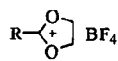


CL 1371 (1985)
CC 119 (1985)
TL 28 4331, 4335 (1987)

$\text{RCH}=\text{NR}'$, cat M(OTf)_3 ($\text{M} = \text{Sc}, \text{Y}, \text{Yb}$)/ H_2O ($\text{E}' = \text{CHRNHR}'$)

SL 233 (1995)

$\text{RCH}=\text{NR}'$, TiX_4 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$)/ H_2O ($\text{E}' = \text{CHRNHR}'$)

TL 3643 (1977); 21 2077, 2081 (1980); 28 227 (1987); 35 3737 (1994); 36 5227 (1995)
Syn 545 (1981)

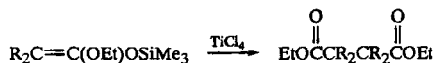
$\text{RCH}=\text{NR}'$, ZnX_2 ($\text{X} = \text{halogen}$, $\text{E}' = \text{CHRNHR}'$)	TL 29 5291 (1988); 35 3737 (1994)
$\text{RCH}=\text{NSiMe}_3$, ZnI_2 ($\text{E}' = \text{CHRNHSiMe}_3$)	CC 539 (1985)
$\text{RCH}=\text{NOCH}_2\text{Ph}$, cat Me_3SiOTf ($\text{E}' = \text{CHRNHOCH}_2\text{Ph}$)	TL 24 4707 (1983)
$\text{R}^1\text{CH}=\overset{\text{O}^-}{\underset{+}{\text{N}}}\text{R}^2$ ($\text{E}' = \text{CHR}^1\text{NR}^2\text{OSiR}_3$)	CL 1787 (1982) TL 28 1431 (1987)
nitro-olefins, TiCl_4 , $\text{Ti}(\text{O}-i\text{-Pr})_4$ (γ -keto esters)	See page 1511, Section 12.
$\text{HC}(\text{OMe})_3$, TiCl_4 [$\text{E}' = \text{CH}(\text{OMe})_2$]	TL 26 4129 (1985) (chiral)
$\text{RC}(\text{OR})_3$, TiCl_4	TL 31 421 (1990)
 BF_4^-	CL 1243 (1987)
 cat $[(\text{Et}_2\text{N})_3\text{S}]\text{Me}_3\text{SiF}_2$ (1,2-addition)	TL 34 7907 (1993)
 O , R_3SiNuc , catalyst	See page 953, Section 5.
pyridines (4-substituted dihydropyridines)	TL 30 747 (1989)
$(\text{H}_2\text{C}=\text{CH})_2\text{SO}_2$, TiCl_4 (1,4-monoaddition)	JOC 54 2247 (1989)
enone (1,4-addition)	See page 1571, Section 2.
$\text{RCH}=\text{CHCO}_2\text{R}$ (1,4-addition)	See page 1809, Section 6.
$\text{ArCR}=\text{CXY}$, $h\nu$ ($\text{X}, \text{Y} = \text{H}, \text{CO}_2\text{R}; \text{H}, \text{CN}; \text{CN}, \text{CN}$) (1,4-addition)	See page 1809, Section 6.
$\text{RCH}=\text{CHCOSR}$, cat SbCl_5 - $\text{Sn}(\text{OTf})_2$ (1,4-addition)	CL 91 (1988)
2-acyl-2-alkenoate ester (1,4-addition)	JACS 102 4262 (1980); 115 5841 (1993)
$\text{HC}\equiv\text{CCO}_2\text{H}$, TiCl_4 ($\text{E}' = \text{CH}=\text{CHCO}_2\text{H}$)	JACS 107 3879 (1985)
$\text{RC}\equiv\text{CCO}_2\text{R}$, cat Fe-montmorillonite (1,2-addition)	TL 30 6341 (1989)
$\text{Pb}(\text{OAc})_4$ ($\text{E}' = \text{OAc}$)	Helv 68 216 (1985)
$(\text{ArSO}_2\text{O})_2$, (NaOMe) ($\text{E}' = \text{O}_3\text{SAr}$)	JOC 53 3855 (1988)
RCONRSAr , Me_3SiOTf ($\text{E}' = \text{SAr}$)	JOC 57 1948 (1992)
ArSO_2F ($\text{E}' = \text{SO}_2\text{Ar}$)	JOC 55 1125 (1990)
PhSeBr	JOC 57 3887 (1992)
EtO_2CN_3 , $h\nu$ ($\text{E}' = \text{NHCO}_2\text{Et}$)	TL 30 2975 (1989)

t-BuO₂CN=NCO₂-*t*-Bu, TiCl₄, [Ti(O-*i*-Pr)₄]
 [E' = N(CO₂-*t*-Bu)NHCO₂-*t*-Bu]

JACS 108 6394 (1986)

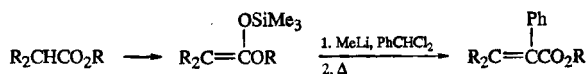
Helv 69 1923 (1986)

For halogenation, see page 732, Section 6.



TL 2009 (1977)

JOC 53 3334 (1988)



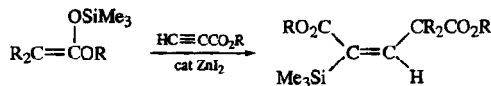
Syn Commun 12 401 (1982)



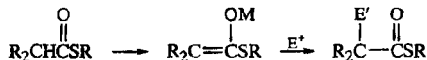
E⁺ = H₂O, D₂O, NCS, NBS, PhSeCl, RCHO, R₂CO

TL 29 6443 (1988)

JOC 57 6890 (1992)



TL 29 6443 (1988)



M

E⁺

Li

RCHO, R₂CO

TL 3255 (1975); 21 3975 (1980); 36 8267 (1995)

JACS 103 3099, 3211 (1981)

Tetr 41 5089 (1985)

JOC 60 7778 (1995)

For β-lactone formation, see page 1861, Section 8.

B

RCHO, R₂CO

TL 2225, 3937 (1979); 25 2283 (1984)

JACS 103 3099 (1981)

Tetr 40 4059 (1984)

JOC 54 2817 (1989) (chiral); 60 3288, 6248 (chiral) (1995)

Angew Int 32 1618 (1993) (chiral)

Si

RCH(OR)₂, cat Me₃SiOTf

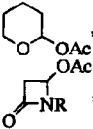


RCH(OR)₂, cat Sc(OTf)₃

RCH(OR)₂, TiCl₄

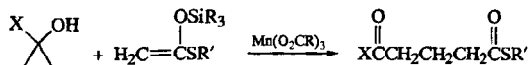
Tetr 37 3899 (1981); 44 4259 (1988)

SL 472 (1993)

JOC 55 6107 (1990)

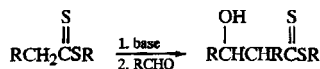
		, cat Me_3SiOTf	TL 23 2601 (1982) Tetr 44 4259 (1988)
		, cat Me_3SiOTf	CC 1076 (1981) TL 25 2793 (1984); 26 673, 4739 (1985); 28 507 (1987) BCSJ 58 3264 (1985) JOC 58 988 (1993); 59 5136 (1994) (enantio-selective) TL 33 1729 (1992)
	RCHO		
	RCHO, cat BH_3 , cat $\text{TsNHCR}^1\text{R}^2\text{CO}_2\text{H}$ (chiral)		TL 26 797, 4129 (1985); 36 6109 (1995) Tetr 42 893 (1986) JOC 54 83 (1989); 57 456 (1992); 60 5910 (1995) SL 165 (1994) CL 297, 1001 (1989)
	RCHO or R_2CO , $\text{BF}_3 \cdot \text{OEt}_2$		
	RCHO, $\text{Sn}(\text{OTf})_2$, <i>n</i> -Bu ₄ NF, chiral diamine (chiral)		
	RCHO, $\text{Sn}(\text{OTf})_2$, chiral diamine (chiral)		CL 1455 (1990) Tetr Asym 2 635 (1991)
	RCHO, $\text{Sn}(\text{OTf})_2$, <i>n</i> -Bu ₂ Sn(OAc) ₂ , chiral diamine (chiral)		CL 1757 (1989)
	RCHO or R_2CO , SnCl_4		TL 26 2373 (1985) Tetr 42 893 (1986) JOC 60 5910 (1995) SL 472 (1993)
	RCHO, cat $\text{Sc}(\text{OTf})_3$		
	RCHO or R_2CO , TiCl_4		TL 26 2373 (1985); 36 6109 (1995) Tetr 42 893 (1986); 44 5965 (1988) JOC 53 4015 (1988); 54 83 (1989); 57 456, 2034 (1992); 58 338, 2946, 7768 (1993) IACS 116 4077 (1994); 117 2363 (1995) SL 1057 (1995)
	RCHO, Ti-BINOL (chiral)		
	RCHO, cat $\text{Yb}(\text{OTf})_3$		Syn 371 (1993)
	RCHO or R_2CO , <i>n</i> -Bu ₄ NF		TL 26 2373 (1985) Tetr 42 893 (1986) CL 2069 (1989) JOC 57 1324 (1992) SL 147 (1994) JOC 57 1324 (1992)
	RCOCO ₂ R, $\text{Sn}(\text{OTf})_2$, <i>n</i> -Bu ₃ SnF, chiral diamine (chiral)		
	RCOCO ₂ R; $\text{BF}_3 \cdot \text{OEt}_2$, EtAlCl_2 , $\text{Sn}(\text{OTf})_2$, SnCl_4 or TiCl_4		
	RCOCO ₂ R, various Lewis acids		SL 855 (1993)
Ti	RCHO		JOC 57 6339 (1992) TL 36 8267 (1995)
Zn			TL 28 507 (1987)
	RCHO		TL 21 3975 (1980)

For reactions with imines to form β -lactams, see page 1861, Section 8.



X = H, R, OR, NR₂, SiR₃, CO₂R; R' = 2-pyridyl

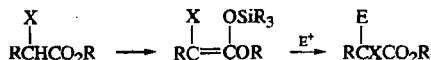
BCSJ 66 819 (1993)



TL 4657 (1978); 22 3925 (1981)

JACS 105 5015 (1983)

Tetr 41 2691, 5089 (1985)



X

E⁺

OR

H⁺ (enantioselective)

TL 35 2891 (1994)

RCHO, Sn(OTf)₂, *n*-Bu₃SnF, chiral diamine (enantioselective)

TL 35 3329 (1994)

RCHO, cat Sn(OTf)₂, cat SnO, chiral diamine (enantioselective)

TL 35 9573 (1994)

RCHO, Sn(OTf)₂, *n*-Bu₂Sn(OAc)₂, chiral diamine (enantioselective)

TL 35 3329 (1994); 36 3173 (1995)

JOC 60 1098 (1995)

SL 675 (1995)

RCHO, *i*-PrOTiCl₃

JACS 116 12111 (1994)

RCHO or R₂CO, ZnCl₂

CC 20 (1985)

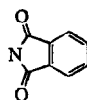
RCH=NCOR/H₃O⁺

JOC 58 5889 (1993)

RCHO, Lewis acid

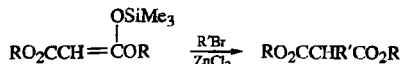
TL 26 6509 (1985)

SMe

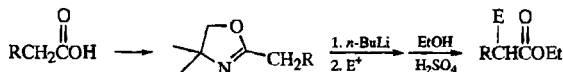


H₂C(OR)₂, TiCl₄

TL 30 1181 (1989) (intramolecular)



JACS 110 482 (1988)



E⁺

RX

JACS 92 6644 (1970); 96 6508 (1974)

JOC 39 2778, 2787 (1974); 46 3097 (1981)

Angew Int 15 270 (1976)

Pure Appl Chem 51 1255 (1979) (asymmetric induction)

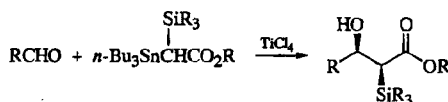
TL 28 5509 (1987)

RCHO

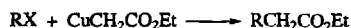
JACS 103 4278 (1981) (B azaenolate)



TL 34 47 (1993)

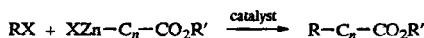


SL 911 (1991)



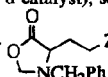
R = allylic, benzylic

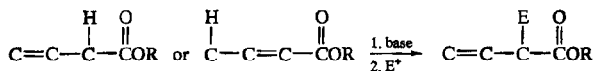
TL 1163 (1972)



<i>n</i>	Catalyst	RX	
1	—	allylic halide, α-halo ester	Syn Commun 13 523 (1983)
	M(PPh ₃) ₄ , M = Ni, Pd	vinyl bromide	JOMC 209 109 (1981)
	Cu(acac) ₂	allyl bromide	TL 24 2749 (1983)
2	NiCl ₂ L ₂	allylic chloride	JACS 109 8056 (1987)
	Pd(PPh ₃) ₄	vinyl triflate	TL 27 955 (1986)
	Pd(PPh ₃) ₄ (LiCl)	aryl triflate	TL 28 2387 (1987)
	PdCl ₂ [(<i>o</i> -Tol) ₃ P] ₂	aryl halide	TL 27 83, 955 (1986)
			JACS 109 8056 (1987)
		vinyl halide	TL 27 83 (1986)
			JACS 109 8056 (1987)
		vinyl triflate	TL 27 955 (1986)
			JACS 109 8056 (1987)
	CuBr·SMe ₂	aryl, vinylic or allylic halide	TL 28 337 (1987)
			JACS 109 8056 (1987)
	CuCN	allylic halide or tosylate	JOC 52 4418 (1987)
3	PdCl ₂ [(<i>o</i> -Tol) ₃ P] ₂	aryl halide, vinylic halide or triflate	TL 27 955 (1986)
	PdCl ₂ (dppf)	aryl and allylic halides	TL 35 1177 (1994)
	Pd(PPh ₃) ₄	aryl halide	JOC 56 1445 (1991)
	CuCN·2LiBr	allylic halide	JOC 56 1445 (1991)
	CuCN	allylic halide or tosylate	JOC 52 4418 (1987)
4	CuCN	allylic tosylate	JOC 52 4418 (1987)

 For RO₂CCH(NHBoc)CH₂ZnI (ArI, Pd catalyst), see TL 30 5941 (1989), TL 35 551 (1994), JOC 57 3397

 (1992) and SL 293 (1994); and for  ZnI (ArX, Pd catalyst), see SL 379 (1994).

 E^+ H_2O or D_2O (See also page 220, Section 2.2.)

TL 4249 (1972); 25 1333, 5177 (Z alkene), 5181 (Z alkene) (1984); 28 5075 (1987); 32 2719, 2723 (1991)

BCSJ 51 2970 (1978)

JACS 102 3964 (1980); 107 1293 (1985); 108 2776 (1986); 109 6389, 8117 (1987)

J Med Chem 23 525 (1980)

Helv 64 1023 (1981) (stereochemistry)

JOC 47 163 (1982) (stereochemistry); 55 2374

(1990) (3-stannyl-2-alkenoate esters); 56 2468 (1991) (2-silyl-2-alkenoate esters)

Syn 129 (1982)

RX

Agric Biol Chem 24 685 (1960); 26 705 (1962); 36 793 (1972)

JACS 94 1790 (1972); 96 5662 (1974); 107 1285, 7184 (1985); 112 5601 (1990)

TL 4249 (1972); 2433 (1973); 4135, 4171 (1975); 4485 (1977); 21 2509 (1980); 22 1691 (1981); 28 6253 (1987); 31 6789 (1990); 32 7281 (1991); 34 5217, 7669 (1993)

JOC 39 2323 (1974); 44 300 (1979); 47 163 (1982); 49 3278 (1984); 51 123, 561 (1986); 52 353, 4471, 4517 (1987); 53 926, 1441, 3947 (1988); 54 3800 (1989); 56 2468, 2849 (1991); 58 3444 (1993); 59 2324, 8203 (1994)

Syn Commun 7 483 (1977)

CC 799 (1980); 502 (1982); 1717 (1986)

Syn 129 (1982)

Chem Pharm Bull 30 4015 (1982) (2-isocyano-2-alkenoate ester)

Org Syn Coll Vol 8 486 (1993)

$\text{RCH}=\text{CHCH}_2\text{Cl}$, cat π -allylpalladium chloride, cat PPh_3

TL 30 2383 (1989)

 RCHO , R_2CO

TL 4249 (1972); 4135 (1975); 35 6611 (1994)
JOC 41 4065 (1976); 45 1181 (1980); 47 163 (1982); 52 3956 (1987); 59 6643 (1994)

JACS 108 3755 (1986); 117 9369 (1995)

SL 275 (1992)

 $\text{RCH}=\text{NR}$

JOC 59 7839 (1994) (Li, Zn enolates)

 $\text{PhCH}=\text{NSiMe}_3$ (lactam formation)

JACS 106 4819 (1984)

 $\text{H}_2\text{C}=\text{C}(\text{SMe})\text{CO}_2\text{Me}$ (1,4-addition)

TL 2603 (1973)

 O_2 , SnCl_2 ($\text{E} = \text{OH}$)

TL 4215 (1976)

(+)-(camphorylsulfonyl)oxaziridine ($\text{E} = \text{OH}$)

JACS 111 8039 (1989); 114 2567 (1992)

 $(\text{PhCO}_2)_2$ ($\text{E} = \text{O}_2\text{CPh}$)

TL 4215 (1976)

 PhSSO_2Ph ($\text{E} = \text{SPh}$)

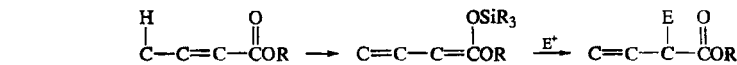
JOC 51 4594 (1986)

MeSSO₃Me (E = SMe)

TL 4215 (1976)

RO₂CN=NCO₂R (E = RO₂CNHNCO₂R)

JOC 55 3118 (1990)



E⁺

HCl

JACS 109 7063 (1987)

[(Me₂N)₃S]F₂SiMe₃ / PhCH₂Br

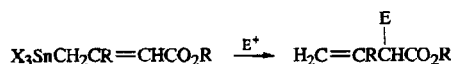
JOC 53 3532 (1988)

H₂C=C(CH₃)NO₂, TiCl₄, Ti(O-*i*-Pr)₄ / H₂O
(E = CH₂COCH₃)

CL 1043 (1980)

RCHO, cat [(Me₂N)₃S]HF₂

JOC 53 3532 (1988)



X

E⁺

Cl

RCHO

JOC 55 3118 (1990)

RO₂CN=NCO₂R

TL 30 3445 (1989)

JOC 55 3118 (1990)

R

RCHO, Lewis acid or *n*-Bu₄NF

CC 561 (1987)

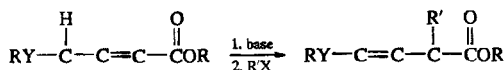
TL 30 5533 (1989)

JOC 55 3118 (1990)

RO₂CN=NCO₂R, ZnCl₂

TL 30 3445 (1989)

JOC 55 3118 (1990)



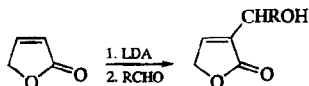
Y

O

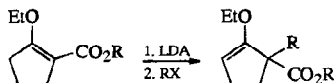
Syn Commun 7 189 (1977)

S

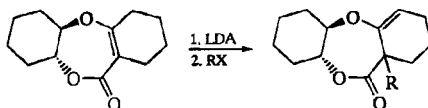
TL 405 (1975); 24 3391 (1983)



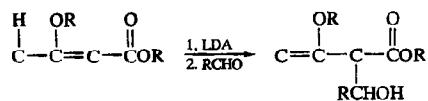
TL 28 985 (1987)



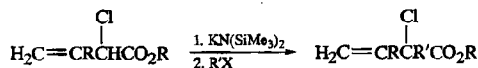
JOC 52 5745 (1987); 57 2585 (1992)



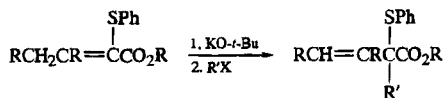
TL 33 3481 (1992)



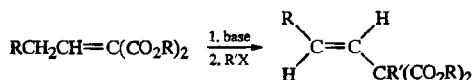
JACS 111 643 (1989)



JOC 55 5294 (1990)



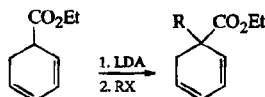
TL 24 2113, 3391 (1983)



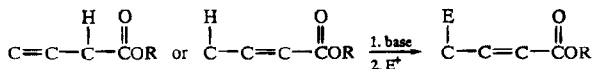
JACS 62 314 (1940)

CL 1909 (1982)

JOC 51 4944 (1986)



JACS 109 6187 (1987)

 E^+ H_2O

BCSI 51 2970 (1978)

JOC 50 3526 (1985)

RX

JACS 94 1790 (1972); 96 5662 (1974); 98 1204 (1976); 107 7184 (1985)

JOC 39 669 (1974)

RCHO, R₂CO

JACS 74 5529 (1952); 77 4111 (1955); 112 4609 (1990); 113 1057 (1991)

J Vitaminol (Osaka) 4 178, 190 (1958) [CA 53 5329b,d (1959)]

Helv 45 528 (1962)

Can J Chem 46 3115 (1968)

TL 1507 (1972); 4135 (1975); 23 4773 (1982); 28 5249 (1987)

Ber 106 2643 (1973); 110 1594 (1977)

Syn 343 (1974)

JOC 45 1181 (1980); 58 2186 (1993); 60 1195 (1995)

$\text{CdCl}_2/\text{RCHO}$

TL 27 5193 (1986)

$\text{RCH}=\text{NR}$

JOC 59 7839 (1994) (Li, Zn enolates)

$(\text{ArSO}_3)_2$, NaOMe or ZnCl_2 ($\text{E} = \text{O}_3\text{SAr}$)

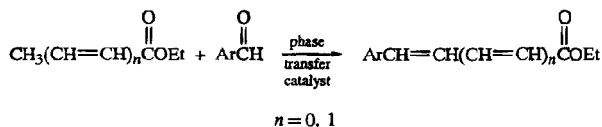
JOC 56 1014 (1991)

PhSeCl

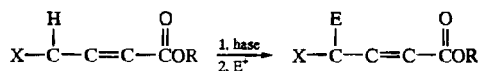
JOC 51 5243 (1986)

$\text{RO}_2\text{CN}=\text{NCO}_2\text{R}$ ($\text{E} = \text{RO}_2\text{CNNHCO}_2\text{R}$)

TL 30 3445 (1989)
JOC 55 3118 (1990)



J Chem Res (S) 106 (1981)



X

E^+

Br

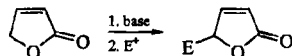
RCHO

TL 1507 (1972)

PhSO_2

RX

BSCF 743, 746 (1973)



E^+

D_2O

TL 1627 (1979)

RX

CC 81 (1979)

RCHO , R_2CO

JOC 39 669 (1974)

JCS Perkin I 70 (1979)

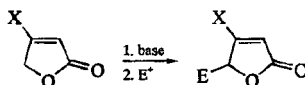
CC 81 (1979)

TL 1627 (1979); 28 985 (1987)

Michael acceptors ($\text{RCH}=\text{CHCOR}$,
 $\text{RCH}=\text{CHCO}_2\text{R}$, $\text{H}_2\text{C}=\text{CHCN}$)

TL 3129 (1977)

JOC 53 3330 (1988)



X

E^+

MeO

D_2O , NBS, RCHO

TL 1627 (1979)

$\text{BF}_3 \cdot \text{OEt}_2 + \text{RCH}(\text{OMe})_2$,

TL 23 5229 (1982)

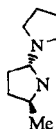
$\text{R}(\text{OMe})_3$ or $\text{C}(\text{OMe})_4$

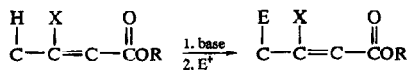
RX

TL 29 1489 (1988) (chiral)

RX, RCHO

CC 81 (1979)



XE⁺

OR

RX

TL 33 3481 (1992)

RCHO, R₂CO

JOC 45 1181 (1980)

NR₂

RX

TL 39 (1973); 3963 (1974)

Syn 401 (1976)

JOC 57 2992 (1992)

RCHO, R₂CO

JOC 45 1181 (1980); 57 2992 (1992)

JACS 104 357 (1982); 107 1777 (1985);

108 3112 (1986); 110 7901 (1988)

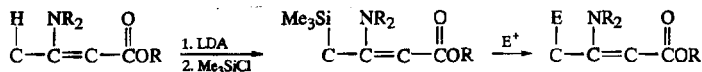
TL 27 6173 (1986) (ZnCl₂ added)

RCOCl

JOC 52 708 (1987)

Me₃SiCl

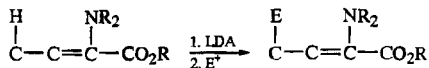
TL 23 3011 (1982)

E⁺RCHO, R₂CO, HC(OMe)₃

TL 23 3011 (1982)

RCOCl

TL 23 3011 (1982); 28 5423 (1987)

E⁺

RX

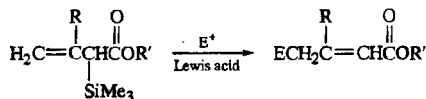
Syn 58 (1983)

RCHO, R₂CO

Syn 61 (1983)

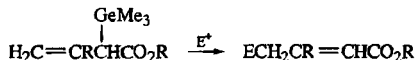
RCHO (ZnCl₂)

JACS 109 1587 (1987)

E⁺ = RX (R = allylic, benzylic), RCHO, R₂C(OMe)₂, R₂CO, RCOCl, PhSCHClR

TL 23 723, 2953 (1982)

CL 961 (1982)



E^+

$PhCHBrMe, ZnBr_2$ JOC 55 3118 (1990)

$RCH=CHCH_2Br, Me_3SiCl$ JOC 55 3118 (1990)

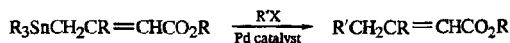
$MeOCH_2Cl, TiCl_4$ JOC 55 3118 (1990)

$RCH(OMe)_2$ or $R_2C(OMe)_2, TiCl_4$ JOC 55 3118 (1990)

$RCHO, TiCl_4$ JOC 55 3118 (1990)

$RO_2CN=NCO_2R, TiCl_4$ TL 30 3445 (1989)

JOC 55 3118 (1989)

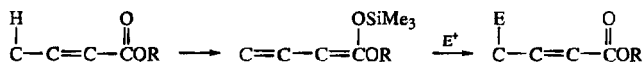


$R'X = ArBr, R_2C=CHBr, RCOCl$

JOC 55 3118 (1990)



TL 30 5533 (1989)


 E^+

$RCHC \equiv CH + Co_2(CO)_8P(OR)_3$ JACS 115 6438 (1993)

$PhSCl, PhSCHClR, RCOCl, RBr$ (R = allylic, benzylic), $MeOCH_2Cl, MeCH(OEt)_2$, or $HC(OMe)_3; ZnBr_2$ TL 3205, 3209 (1979)

 $, ZnBr_2$ ($X = S, Se$) TL 24 5911 (1983)

$HC(OMe)_3, ZnBr_2$ TL 26 397 (1985)

$RCHO, cat [(Me_2N)_3S]HF_2$ JOC 53 3532 (1988)

$RCHO, TiCl_2(O-i-Pr)_2$ JACS 115 4497 (1993)

$RCOCl, ZnBr_2$ JOC 52 708 (1987)

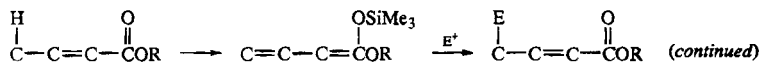
$RCH=NR, TiCl_4$ TL 28 613 (1987) (5,6-dihydro-1H-pyridin-2-ones or 5-amino-2-alkenoate esters)

iminium salts JACS 113 6161 (1991)

$RCH=N^+R, Me_3SiOTf$ [$E = CHRNR(OSiMe_3)$] TL 36 7293 (1995)

quinone

CC 102 (1987)
TL 29 85 (1988)

 E^+ $(\text{ArSO}_2\text{O})_2$, NaOMe or ZnCl_2 ($\text{E} = \text{ArSO}_3$)

JOC 56 1014 (1991)

 $\text{RO}_2\text{CN}=\text{NCO}_2\text{R}$, TiCl_4

TL 30 3445 (1989)

JOC 55 3118 (1990)

 PCl_3

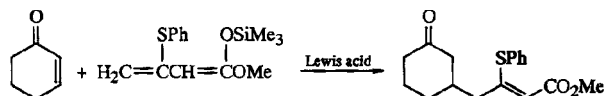
TL 31 1147 (1990)

 AsCl_3

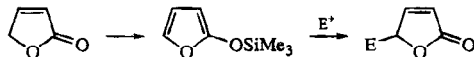
TL 31 1147 (1990)



JACS 117 12360 (1995)



See page 1571, Section 2.

 E^+ 1°RI , AgO_2CCF_3

Helv 72 1362 (1989)

allylic halide, AgO_2CCF_3

TL 28 949 (1987); 31 5741 (1990)

SL 745 (1990)

allylic alcohol, LiClO_4

JOC 57 2986 (1992)

 $\text{CF}_3\text{CH}(\text{OH})\text{OEt}$, ZnI_2

TL 33 1351 (1992)

 $\text{RCH}(\text{OMe})_2$ or $\text{R}_2\text{C}(\text{OMe})_2$, SnCl_4

TL 22 4269 (1981)

 $\text{RCH}(\text{OMe})_2$, TiCl_4

TL 35 4685 (1994)

 RCHO , cat $n\text{-Bu}_4\text{NF}\cdot\text{silica}$

Heterocycles 19 2327 (1982)

 RCHO , $\text{BF}_3\cdot\text{OEt}_2$

TL 30 5325 (1989); 35 4685, 5769 (1994); 36 7175 (1995)

JOC 55 2565 (1990); 56 2135, 6523 (1991)

 RCHO , R_3SiOTf

TL 35 7897 (1994)

 RCHO , $\text{TiCl}_2(\text{O}-i\text{-Pr})_2$

TL 34 6081 (1993)

 RCHO or R_2CO ; $\text{BF}_3\cdot\text{OEt}_2$, ZnCl_2 , ZnBr_2 , CsF ,
 $n\text{-Bu}_4\text{NF}$, $(\text{Ph}_3\text{C})\text{ClO}_4$ or $\text{R}'_3\text{SiOTf}$ ($\text{R}' = \text{Me}$, Et)

TL 28 4037, 4041 (1987)

 RCHO or R_2CO , SnCl_4


TL 21 4611 (1980); 22 4269 (1981); 28 985, 4037, 4041 (1987)

JACS 114 383 (1992)

HC(OR)₃, cat SnCl₄ BCSJ 52 1953 (1979)

RC(OR)₃, cat Lewis acid BCSJ 52 1953 (1979)

RCHCl(OAc), cat SnCl₄ BCSJ 52 1953 (1979)

 OAc, cat (Ph₃C)ClO₄ TL 34 8093 (1993)

RCH(SPh)OAc, SnCl₄ (E = CHRSPH) TL 36 2101 (1995)

XCHRNHCO₂R (X = OH, OMe), BF₃·OEt₂ TL 32 3795 (1991)
(E = CHRNHCO₂R)

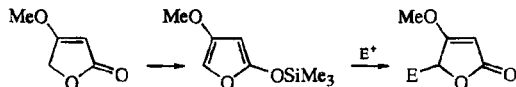
 OMe, Lewis acid TL 34 5773 (1993)
CO₂R

 O₂-t-Bu, cat Me₃SiOTf SL 1221 (1995)
CO₂R

RCH=NR, BF₃·OEt₂ JOC 55 2565 (1990); 58 3397 (1993)

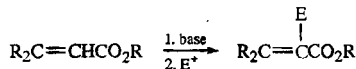
enone, n-Bu₄NF (1,4-addition) TL 30 6491 (1989)

Pb(OAc)₄ (E = OAc) BCSJ 53 1061 (1980)

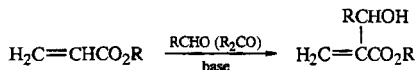


E⁺ = ZnBr₂ or TiCl₄ plus RCH(OMe)₂, RC(OMe)₃, C(OMe)₄, RCHO or R₂CO; Br₂; Pb(OAc)₄ (E = OAc)

TL 23 353 (1982)



See page 351, Section 1.



JCS Perkin I 2079 (1982); 2293 (1983)

Angew Int 22 795, 796 (1983)

Helv 67 413 (1984)

JOC 50 3849 (1985); 53 3701 (1988); 58 2151 (1993); 60 6515 (1995)

TL 27 5007 (1986); 28 4351 (1987) (RCOCO₂R); 30 6337 (1989); 31 1621 (1990); 32 5611 (1991); 33 1045

(1992) (intramolecular); 34 7049 (1993); 35 1371 (1994); 36 8107 (1995)

Tetr 44 4653 (1988) (review)

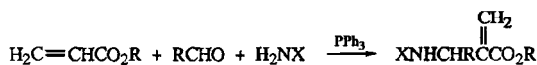
J Chem Res (S) 330 (1988) (high pressure)

Syn Commun 18 495 (1988); 21 2269 (1991); 23 1261 (ultrasound); 2807 (intramolecular) (1993)

Tetr Asym 2 969 (1991) (chiral)

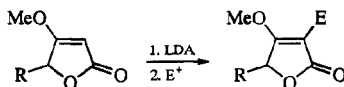
Org Syn Coll Vol 8 420 (1993)

SL 444 (1994) (microwave); 607 (1995)



$\text{X} = \text{CO}_2\text{R}, \text{Ts}$

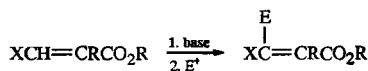
TL 30 2731 (1989)



$\text{E}^+ = \text{MeOD}, \text{MeI}, \text{RCHO}, (\text{RCO})_2\text{O}, \text{RCO}_2\text{R}, \text{RSSR}, (\text{RCO}_2)_2$

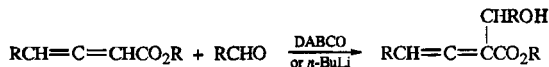
Angew Int 21 637 (1982)

TL 23 581, 585, 1793 (1982)

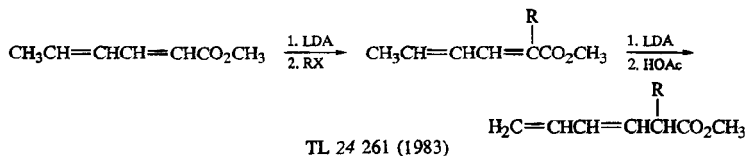


$\text{X} = \text{Ph}, \text{OR}, \text{SR}, \text{NR}_2, \text{CO}_2\text{R}$

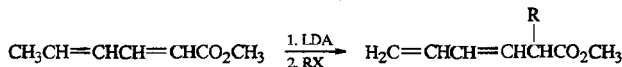
See page 351, Section 1.



JOC 58 5952 (1993)

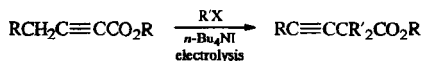


TL 24 261 (1983)

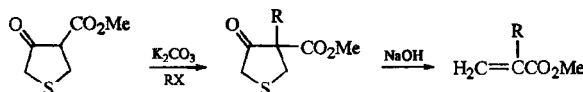


JOC 48 3003 (1983)

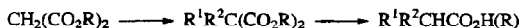
TL 31 4697 (1990)



CC 188 (1980)



CC 1265 (1982)



Review: Org Rxns 9 107 (1957)

Alkylation

base / RX

Org Syn Coll Vol 1 250 (1941); 2 474 (1943); 3 495, 705 (1955); 4 288 (1963); 7 411 (1990); 8 5, 381 (1993)

JACS 80 622 (1958); 106 1051 (1984) (intramolecular); 109 7477 (1987); 110 1547, 6210 (intramolecular) (1988); 112 363 (1990)

JCS B 67 (1968) (intramolecular)

JOC 43 4682 (1978); 46 3127 (1981) (intramolecular); 47 3769 (1982); 53 3841 (1988)

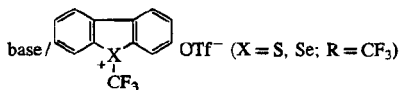
CC 522 (1979)

Rec Trav Chim 99 96 (1980)

J Chem Res (S) 283 (1980)

Syn 452, 805, 893 (1982); 54 (1985)

TL 29 1565, 1577 (1988) (both peptides)



TL 31 3579 (1990)

JACS 115 2156 (1993)

ROMs, CsF

JOC 60 2627 (1995)

3° RCl, BF₃·OEt₂

Naturwiss 51 288 (1964)

BF₃ / RCl

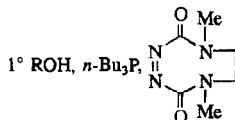
TL 3599 (1966)

1° ROH, *n*-Bu₃P=CHCN

TL 36 2531 (1995)

1° ROH, *n*-Bu₃P, Me₂NCON=NCONMe₂

TL 36 2531 (1995)



TL 36 2531 (1995)

RCH=CH₂, PdCl₂(PhCN)₂, Et₃N / CO, MeOH
(R¹ = CHRCH₂CO₂Me)

JACS 112 6255 (1990)

AllylationH₂C=CHCH₂SiMe₃, CAN

JOC 60 856 (1995)

base / H₂C=CHCH₂OAc, cat Fe₂(CO)₉

JOMC 285 C13 (1985)

base / H₂C=CHCH₂OCO₂Et, cat *n*-Bu₄N-
[Fe(CO)₃NO]

JOC 52 974 (1987)

H₂C=CHCH₂X (X = OAc, O₂SPh), cat NiCl₂L₂

JOMC 250 C21 (1983)

allene, cat Pd(DBA)₂, cat dppe

TL 36 3853 (1995)

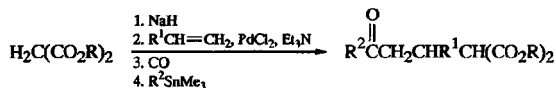
via π -allyl Pd compounds

Tetr 33 2615 (1977)

J. Tsuji, "Organic Synthesis with Palladium Compounds," Springer, New York (1980) (review)

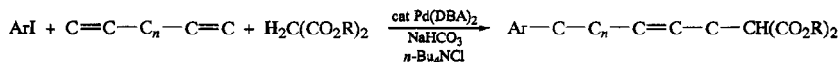
- Acct Chem Res 13 385 (1980)
 Pure Appl Chem 54 189 (1982) (chiral)
 R. Heck, "Palladium Reagents in Organic Syntheses," Academic Press, New York (1985)
 (review)
 JOC 52 5430 (1987); 54 2759 (1989); 55 791, 4840
 (chiral) (1990); 60 2016 (1995)
 TL 29 2959 (1988) (chiral); 31 3905 (1990) (chiral);
 32 5089 (1991) (chiral); 33 8001 (1992); 34 179,
 1769 (chiral), 2015 (chiral), 3149 (chiral), 6333,
 7793 (chiral), 8135 (chiral) (1993); 35 1523, 2791,
 4631, 6689 (all chiral), 8013, 8597 (chiral) (1994);
 36 461 (chiral), 6305, 8035 (chiral) (1995)
 SL 558, 715 (1992); 551 (1994) (chiral); 1174
 (1995)
 Org Syn Coll Vol 8 5 (1993)
 JACS 116 4062, 4089 (1994) (both chiral); 117 7247
 (1995) (chiral)
 JACS 104 5543 (1982); 105 3343 (1983); 109 1469
 (1987); 112 9590 (1990); 117 6130 (1995)
 Organomet 2 1687 (1983)
 TL 29 1231 (1988)
 JOC 55 1127 (1990)
 JACS 105 7757 (1983); 109 2176 (1987)
 TL 29 1231 (1988)
 JOC 53 4419 (1988)
 TL 36 5211 (1995)
 TL 29 1343 (1988)
 via π -allyl Mo compounds
 via π -allyl W compounds
 via π -allyl Fe compounds
 via $(\eta^5\text{-pentadienyl})(\text{tricarbonyl})\text{iron(I)}$ cations
Benzylation
 ArCHROAc , cat $\text{Pd}(\text{DBA})_2$, cat dppe
 $p\text{-AcOCH}_2\text{C}_6\text{H}_4\text{OAc}$, Cs_2CO_3
 TL 33 2509 (1992)
 TL 33 5287 (1992)
Alkenylation
 TsCH=CHCOX ($\text{X}=\text{OR}$, NR_2)
 TL 30 173 (1989)
Arylation
 ArH , $\text{Mn}(\text{OAc})_3$
 ArH , CAN
 $\text{ArPb}(\text{OAc})_3$
 JOC 54 2703 (1989)
 TL 27 2763 (1986)
 TL 21 965 (1980)
 Austral J Chem 37 1245 (1984)
 NaH/ArX , CuBr(I)
 CL 367 (1981)
 JOC 56 2914 (1991)
 TL 33 4699 (1992)
 JACS 116 3988 (1994)

KO- <i>t</i> -Bu / Ar ₂ IX (X = Cl, Br, I)	JOC 52 4115 (1987) (Meldrum's acid)
KO- <i>t</i> -Bu / <i>o</i> -NC-Ar-Br, NH ₃ , hv	Tetr 38 3479 (1982)
Acylation	
RCOCl, MgCl ₂ , 2 Et ₃ N	JOC 50 2622 (1987)
RCOCl, base	Syn 451 (1982) Syn Commun 12 19 (1982) (both Meldrum's acid)
base / RCOPO(OEt) ₂	CL 1087 (1981)
ArI, CO, Pd catalyst	TL 27 4745 (1986)
Decarboxylation	
~500 °C	JOC 29 1249 (1964)
Δ, CuCl, chiral alkaloid (enantioselective)	TL 28 539 (1987)
hydrolysis / Δ, Cu ₂ O	Syn 1029 (1986)
DABCO, Me ₂ S, Celite, Δ	JACS 109 3010 (1987)
(Me ₄ N)OAc, DMSO	JACS 98 6188 (1976)
(Me ₄ N)OAc, HMPA	JACS 98 630 (1976); 100 3426 (1978)
HCO ₂ H, Et ₃ N, cat Pd(OAc) ₂ , cat PPh ₃ (R = allyl)	JOC 54 5395 (1989)
(Et ₃ NH)O ₂ CH, cat Pd(OAc) ₂ , cat PPh ₃ (R = allyl)	TL 35 2271 (1994)
(Ph ₄ P)Br, <i>n</i> -C ₁₇ H ₃₅ CO ₂ H, 170–200 °C	Syn 320 (1985)
OH ⁻ / H ⁺ / Δ	Org Syn Coll Vol 2 416, 474 (1943); 3 495 (1955); 4 630 (1963) Org Rxs 9 107 (1957) (review)
OH ⁻ / H ⁺ / Δ, amine	TL 34 1995 (1993)
OH ⁻ / H ⁺ / enzyme (enantioselective)	JACS 112 4077 (1990)
B ₂ O ₃ , 170–190 °C	Syn Commun 9 609 (1979)
water, salts, dipolar aprotic solvent	Syn 805 (1982) (review)
H ₂ O, DMSO	TL 1091, 1095 (1974) JOC 43 138 (1978)
LiCl, H ₂ O, DMSO	JOC 43 138 (1978)
NaCl, H ₂ O, DMSO	TL 957 (1973); 1091 (1974); 28 171 (1987); 35 3441 (1994) JOC 43 138 (1978); 52 3205 (1987)
NaCN, LiI, H ₂ O, DMF	JACS 100 3426 (1978); 107 2033 (1985)
NaCN or KCN, DMSO, (H ₂ O)	TL 215 (1967); 35 3441 (1994) Tetr 26 5437 (1970) JOC 43 138 (1978) JACS 107 1421 (1985)
Me ₂ SiI	Syn Commun 9 233 (1979)



$\text{R}^2 = \text{aryl, alkynyl, vinylic}$

JOC 56 5666 (1991)



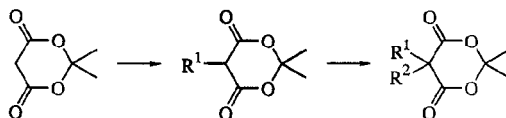
JOC 56 4589 (1991)



JOC 56 3912 (1991); 58 7923 (1993)



JOC 56 4439 (1991)

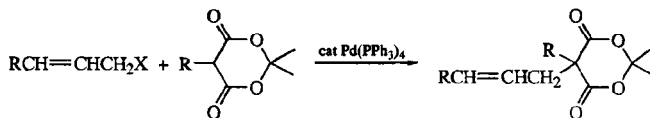


monoalkylation

Chem Ind 786 (1976)

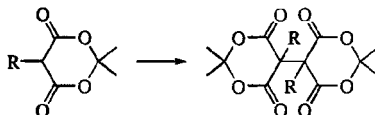
dialkylation

Chem Ind 786 (1976); 809 (1982)

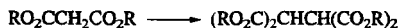


$\text{X} = \text{OAc, O}_2\text{CCF}_3, \text{OCO}_2\text{Et}$

SL 161 (1992)



See page 77, Section 1.



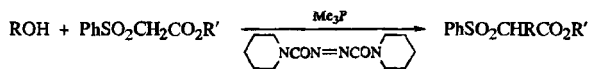
See page 77, Section 1.

Arylation

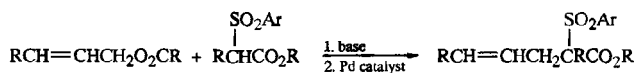
K_2CO_3 , C_6F_6	Org Syn Coll Vol 6 87 (1988)
NaH/ArX	JOC 59 6796 (1994)
base / ArX , electrolysis	TL 30 1373 (1989)
NaH/ArX , CuI , $HMPA$	CL 193 (1983)
ArI , K_2CO_3 , cat CuI , $DMSO$	JOC 58 7606 (1993)
ArI , $KO-t-Bu$, cat $PdCl_2(PPh_3)_2$	Syn 506 (1985)

Decarbalkoxylation

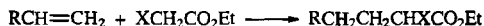
H_2O , $DMSO$	TL 1095 (1974)
water, salts, $DMSO$	Syn 893 (1982) (review)
H_2O , $NaCl$, $DMSO$, Δ	TL 957 (1973); 27 3353 (1986) Syn 893 (1982) (review)
H_2SO_4 , $HOAc$	Org Syn Coll Vol 6 873 (1988)
HCO_2H , Et_3N , cat $Pd(OAc)_2$, cat PPh_3 ($R' = \text{allyl}$)	JOC 54 5395 (1989)



SL 1127 (1995)

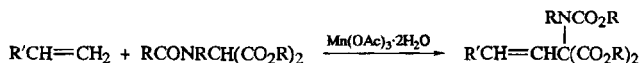


See page 386, Section 21.

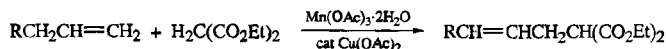


Review: Syn 99 (1970)

<u>X</u>	<u>Reagent(s)</u>	
CO_2Et	$Mn(OAc)_3 \cdot 2H_2O$	CC 693 (1973)
CO_2Et , CN	CuO , Cu_2O , NiO_2 , PbO_2 , MnO_2 , AgO or Ag_2O $(PhCO_2)_2$ or $(t-BuO)_2$	Syn 454 (1977) BSCF 2415, 2417 (1969) (intramolecular)
CN	$(PhCO_2)_2$	BSCF 1109 (1964) Org Syn Coll Vol 6 586 (1988) (intramolecular)

 $R' = \text{aryl, vinylic}$

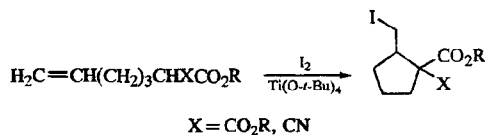
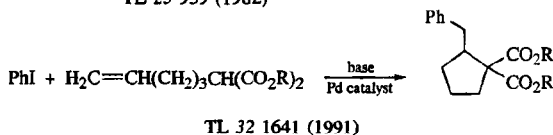
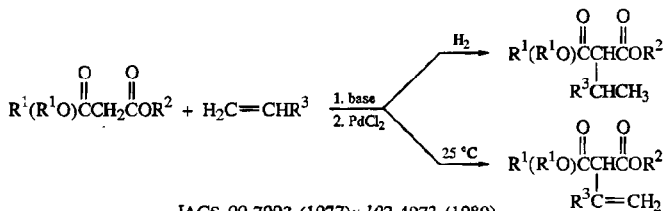
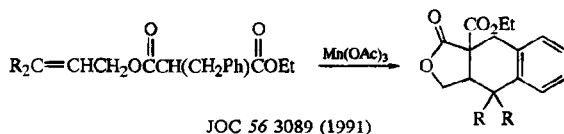
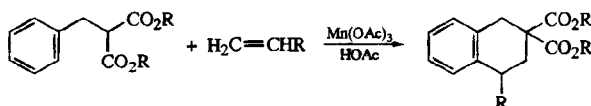
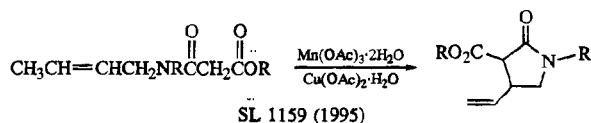
TL 34 7981 (1993)



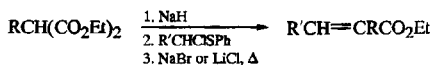
CC 693 (1973)

TL 34 1701 (1993)

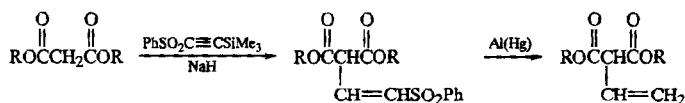
JOC 60 6176 (1995) (intramolecular)



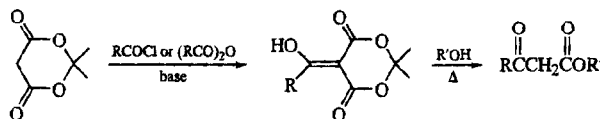
TL 33 2167 (1992)



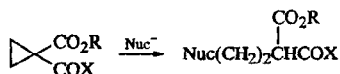
Syn 131 (1982)



JOC 47 4713 (1982)



See page 1528, Section 22.



X = R, OR

Review: *Acct Chem Res* 12 66 (1979)Nuc⁻R₂CuLi

JACS 94 4014 (1972)

TL 997 (1972); 529 (1975); 3857 (1976)

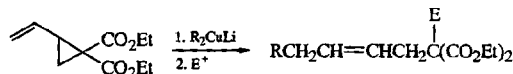
Can J Chem 60 825 (1982)

Ar₂Cu(CN)Li₂ (only X = OR)

TL 35 5373 (1994)

Et₂AlCN (Nuc = CN)

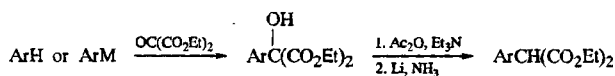
Can J Chem 60 825 (1982)

E⁺H₂O

TL 997 (1972)

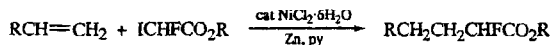
RX

JOC 38 2100 (1973)

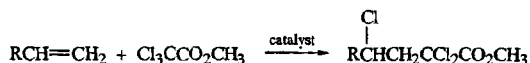


M = Li, MgX

JOC 47 4692 (1982)



TL 33 2137 (1992)

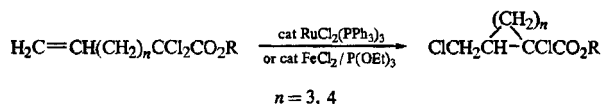
Review: *Syn* 145 (1977)

Catalyst

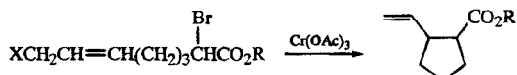
$\text{RuCl}_2(\text{PPh}_3)_3$ JOC 41 396 (1976)

RuCl_2L_3 (polymer) TL 30 3913 (1989)

CuCl JOC 29 2104 (1964)

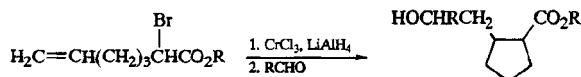


JACS 110 5533 (1988)

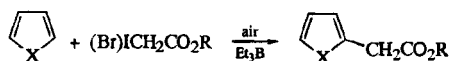


$\text{X} = \text{OH}, \text{OAc}$

SL 743 (1992)

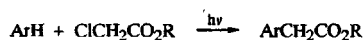


SL 743 (1992)

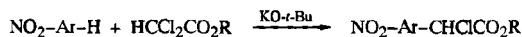


$\text{X} = \text{O}, \text{S}, \text{NR}$

TL 34 5015 (1993)



TL 35 5117 (1994)



SL 181 (1991)



X

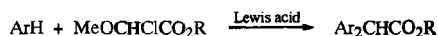
OMe

TL 32 6171 (1991)

SMe

Chem Pharm Bull 30 915 (1982)

SL 49 (1994)



TL 32 6171 (1991)



$\text{RB} \bigcirc$, $\text{NaO}-t\text{-Bu}$

JACS 111 1754 (1989)

R_3B or $\text{RB} \bigcirc$, $\text{KO}-t\text{-Bu}$ ($\text{R}^1 = \text{H}, \text{Br}, \text{alkyl}$;
 $\text{R} = \text{alkyl}, \text{aryl}$)

JACS 90 818, 1911 (1968); 91 2146, 4304 (1969)

R_3B or $\text{RB} \bigcirc$, $2,6-(t\text{-Bu})_2\text{C}_6\text{H}_3\text{OK}$

JACS 91 6855 (1969) ($\text{R}^1 = \text{H}, \text{Br}$; $\text{R} = \text{alkyl}$)
Organomet Chem Syn 1 95 (1970) ($\text{R}^1 = \text{CN}$,
 $\text{R} = \text{alkyl}$)

$\text{RCH}=\text{CHB} \bigcirc$, $2,6-(t\text{-Bu})_2\text{C}_6\text{H}_3\text{OK}$

JOC 51 3398 (1986)

$\text{Zn}/\text{R}_3\text{CX}$ or ArCH_2X

TL 35 555 (1994)

Zn/ArX , Ni or Pd catalyst ($\text{R} = \text{Ar}$, $\text{R}^1 = \text{H}$)

JOMC 132 C17 (1977); 177 273 (1979)

$\text{Zn}/\text{RCH}=\text{CHCHROAc}$, cat $\text{Pd}(\text{PPh}_3)_4$

TL 27 4223 (1986)

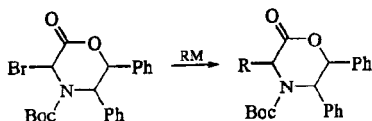
PhCdCl ($\text{R}^1 = \text{H}$)

JOC 33 1675 (1968)



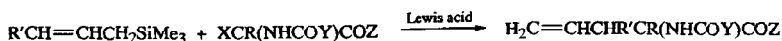
$\text{X} = \text{Cl}, \text{Br}$

TL 27 2435 (1986); 29 1265 (1988)
Syn 223 (1987)

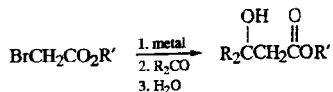


$\text{RM} = \text{H}_2\text{C}=\text{C}(\text{OEt})\text{OSiR}_3$ (ZnCl_2), allylic silane (ZnCl_2), enol silane (ZnCl_2),
arene (ZnCl_2), MeZnCl , $n\text{-Bu}_2\text{Cu}(\text{CN})\text{Li}_2$, Ar_2CuLi , malonate, PhS^-

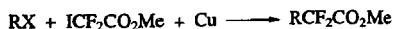
JACS 110 1547 (1988)
JOC 55 3723 (1990)



See page 365, Section 7.

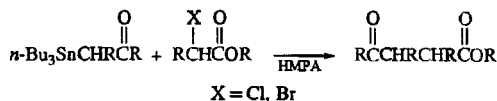


See page 1125, Section 2.1.

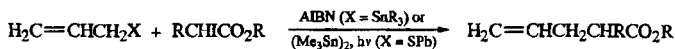


$\text{R} = 1^\circ \text{ alkyl, allylic, benzylic, aryl, alkynyl, vinylic, heterocyclic}$

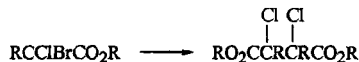
TL 27 6103 (1986)



JCS Perkin I 859 (1993)

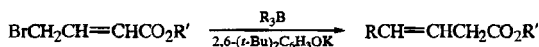


SL 25 (1992)

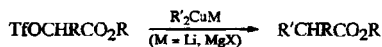


CuBr, LiOMe TL 35 7263 (1994)

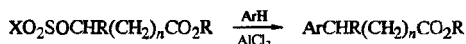
CuBr, Fe TL 36 1103 (1995)



JACS 92 1761 (1970)

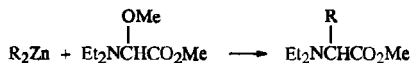


TL 31 2149 (1990)

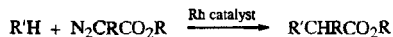


$n = 0, 1; \text{X} = \text{Cl, Me, CF}_3, \text{Ar}$

JOC 50 3945 (1985); 56 183 (1991)



JOMC 256 193 (1983)

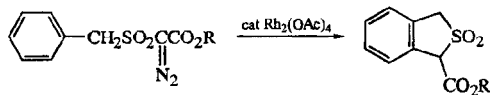


CC 688 (1981)

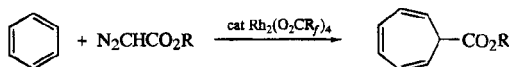
TL 23 4321 (1982); 30 1749 (1989)

JOC 57 436 (1992) (intramolecular)

For intramolecular examples leading to lactones and lactams, see also page 1861, Section 8.

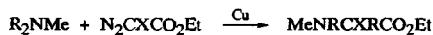


TL 27 5679 (1986)



JOC 46 873 (1981)

For intramolecular examples leading to lactones and lactams, see page 1861, Section 8.



X = H, CO₂Et

Syn 977 (1993)

JOC 59 6051 (1994) (intramolecular)



E⁺

Organometallic

H₂O

R₃B

JACS 90 6891 (1968)

TL 36 2851 (1995)

R₂BCl

JACS 94 3662 (1972)

RBCl₂

JOC 38 2574 (1973)

RCH=CHBCl₂

SL 684 (1991)

(RC≡C)₃B

Can J Chem 50 1105 (1972)

PhCu

JACS 90 2186 (1968)

CC 515 (1969)

D₂O

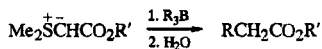
R₃B

JACS 91 6195 (1969)

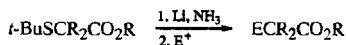
NCS, NBS

R₃B

Can J Chem 50 2387 (1972)

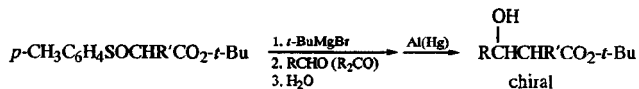


JACS 89 6804 (1967)



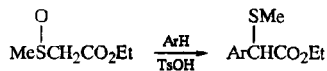
E⁺ = H₂O, RX, RCHO, RCOCl

Syn Commun 3 265 (1973)

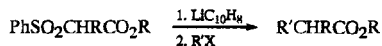


Tetr 36 227 (1980)

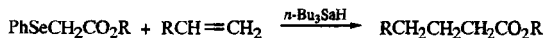
Helv 65 1602 (1982)



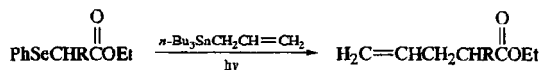
TL 22 81 (1981)



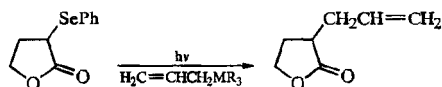
TL 31 1897 (1990)



TL 31 227 (1990)



JACS 110 4815 (1988)


 $\text{R}_3\text{M} = n\text{-Bu}_3\text{Sn}, \text{Ph}_3\text{Pb}$

TL 33 4037 (1992)


 X

H

TL 33 6953 (1992)

 COCH_3

TL 33 6953 (1992)

 COR

CC 354 (1991) (intramolecular)

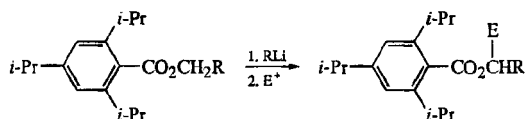
 CO_2R

TL 31 5697 (1990)

CC 354 (1991) (intramolecular)

 CONR_2

CC 354 (1991) (intramolecular)

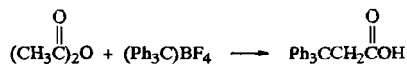

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{Me}_3\text{SiCl}, n\text{-Bu}_3\text{SnCl}$

JACS 99 5213 (1977)

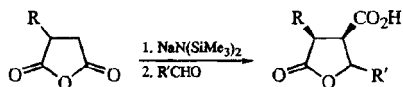
JOC 43 4255 (1978); 46 2363 (1981)

Chem Rev 78 275 (1978) (review)

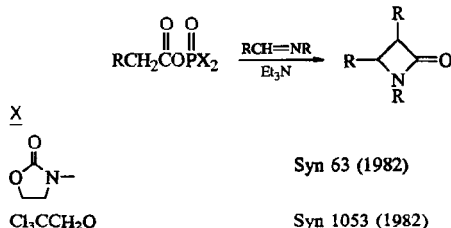
3. Anhydrides



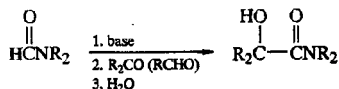
JOC 35 278 (1970)



TL 36 8225 (1995)



4. Amides and Carbamates



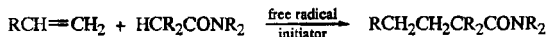
Angew Int 12 836 (1973); 15 293 (1976); 20 795 (1981)

Can J Chem 52 185 (1974)

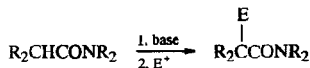
CC 387 (1976)

JCS Perkin I 1881 (1977)

Chem Rev 78 275 (1978) (review)



Syn 99 (1970) (review)



Review: Syn 509 (1977) (polyalkali metal amides)

E^+

H^+

RX

JACS 113 5483 (1991) (chiral); 116 2175 (1994) (chiral)

JOC 26 3696 (1961); 31 982, 989, 3873 (1966); 39 2475 (1974); 42 1688 (1977); 51 1541, 1936 (lactam), 3140 (lactam), 4080 (intramolecular) (1986); 56 872 (1991) (chiral); 57 2531, 2771 (chiral) (1992); 59 1418 (1994)

Ber 101 3113 (1968)

Organomet Chem Syn 1 237 (1971)

Can J Chem 50 3196 (1972) (lactam); 54 1098 (1976)

Ann 369 (1974)

TL 3961 (1978); 21 4233 (1980); 25 857 (1984) (chiral); 28 651 (chiral), 2041, 6389 (1987); 32 1379, 1577 (lactam intramolecular), 2533, 5749 (chiral) (1991); 34 2477, 7701 (chiral lactam) (1993); 35 973 (chiral lactam), 7223 (chiral), 8915 (chiral, on polymer) (1994); 36 6131 (1995) (chiral lactam)

- JOMC 177 5 (1979) (chiral)
 Pure Appl Chem 53 1109 (1981) (chiral)
 JACS 107 3915, 7776 (chiral lactam) (1985); 108 306 (1986) (chiral lactam); 109 4405 (1987) (lactam); 111 1073 (1989) (lactam); 115 9421 (1993); 116 9361 (1994) (chiral)
 CC 992 (1987)
 SL 501 (1990); 33 (1992)
- ArX, hv
 JOC 45 1239 (1980); 54 5983 (1989) (lactam)
 JACS 102 3646 (1980); 107 435 (1985) (both intramolecular)
- ArBr, LiNR₂
 JOC 52 2110 (1987)
- $\begin{array}{c} \text{SO}_2 \\ | \quad | \\ \text{O} \quad \text{O} \\ | \quad | \\ \text{RCHCH}_2 \end{array}$
 JOC 59 520 (1994)
- epoxide
 JOC 37 1907 (1972); 42 1688 (1977); 46 2831 (1981); 57 2771 (1992) (chiral)
 Ber 105 1621 (1972)
 Can J Chem 55 266 (1977)
 JACS 107 7776 (1985) (chiral lactam); 113 6639 (1991) (intramolecular)
 TL 29 4245 (1988); 35 673 (1994)
- RCHO, R₂CO
 Ber 101 3113 (1968)
 Can J Chem 50 3196 (1972) (lactam); 55 266 (1977)
 JOC 39 2475 (1974); 42 1688 (1977); 45 1068 (1980); 50 3019 (1985) (enones); 53 3936 (1988); 58 245 (1993); 59 7346 (1994) (B enolate)
 Ann 369 (1974)
 Syn 954 (1979); 247 (1980)
 TL 21 3975 (1980); 24 3883 (1983); 26 5807 (1985) (chiral Li, Zr enolates); 28 651 (Zr enolate), 2037 (Ti enolate), 6137 (1987); 31 271 (1990); 32 1379, 2525, 2533 (1991); 36 6131 (1995) (chiral lactam)
 Pure Appl Chem 53 1109 (1981) (chiral Li, B, Zr enolates)
 JACS 103 2876 (1981) (chiral Li, Zr enolates); 105 1667 (1983) (diastereoselectivity); 112 2767 (1990) (chiral Li, B, Sn enolates); 115 4602 (1993) (enone)
 Angew Int 22 788 (1983)
 CC 992 (1987)
 SL 501 (1990); 313 (1992) (chiral base, lactam)
- enones (1,4-addition)
 JOC 50 3019 (1985); 57 2531 (1992)
- RCH=CHCO₂R (1,4-addition)
 See page 1809, Section 6.
- RCH=CHNO₂ (1,4-addition)
 See page 1511, Section 12.
- RCOCl
 TL 25 6015 (1984)
 JACS 112 4351 (1990); 117 8258 (1995)
 Org Syn Coll Vol 8 326 (1993)

E^+ RCO_2R

Can J Chem 50 3196 (1972) (lactam)
 TL 29 2521 (1988)
 JOC 58 7277 (1993)
 Org Prep Proc Int 26 249 (1994) (lactams)

 RO_2CCO_2R

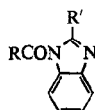
TL 32 1379 (1991)

diketene

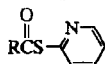
TL 28 4901 (1987) (lactam)



CC 1447 (1986)



SL 728 (1993)



SL 727 (1990)
 JACS 115 9842 (1993)

 RCO_2CO_2Et

Syn 954 (1979)

 $ClCO_2R$

TL 28 4901 (1987); 31 283 (1990)

 CO_2

JOC 58 245 (1992)

 $RSO_2N\begin{array}{c} \diagup O \diagdown \\ \text{chiral, } E = OH \end{array}CR_2$

JOC 51 2402 (1986)

MeSSMe

JOC 42 3236 (1977)

 $PhSSO_2Ph$ ($E = SPh$)

JACS 112 9601 (1990)

 $PhSeBr$

TL 32 1379 (1991)

 $PhSeSePh$

JACS 108 306 (1986) (chiral lactam)

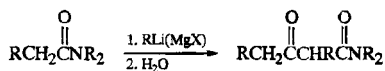
 TsN_3 ($E = N_3$)

Ann 369 (1974)

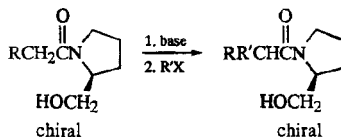
 R_3SiCl

SL 313 (1992) (chiral base)

For the halogenation of amides, see page 736, Section 7.

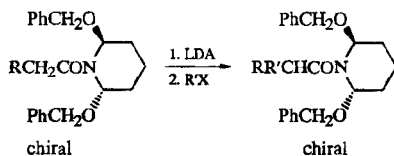


Tetr 38 557 (1982)

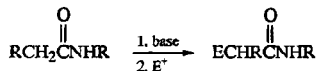


TL 21 4233 (1980)

JOC 45 3137 (1980); 55 5938 (1990); 56 2476 (1991); 59 3347 (1994)



JOC 55 6241 (1990)

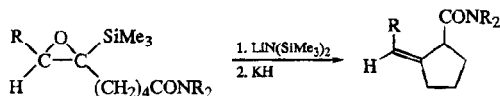

 E^+

RX

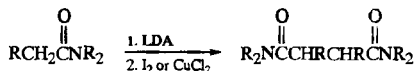
JOC 60 3795 (1995)

 epoxide, $\text{BF}_3 \cdot \text{OEt}_2$

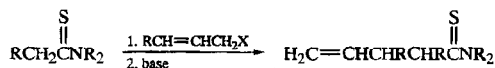
Syn Commun 18 1159 (1988)



JOC 54 2043 (1989)



TL 34 4457 (1993)



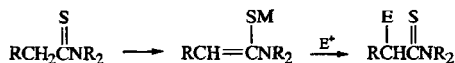
CC 776 (1976)

JACS 98 7084 (1976); 114 10232 (1992)

TL 2167 (1978); 23 881 (1982); 36 8467 (1995)

JOC 45 3729 (1980)

CL 529 (1982)


 M
 E^+

Li

 $\text{RCH}=\text{CHCH}_2\text{X}$
 ArNCO

JOC 48 3631 (1983)

Syn 1063 (1986)

 Li, MgX
 RCHO , R_2CO

JACS 102 7806 (1980)

JOMC 208 279 (1981)

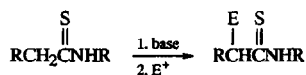
 MgX
 $(\text{RO})_2\text{CO}$

JOC 54 4419 (1989)

Si

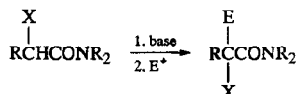
 RCHO , $n\text{-Bu}_4\text{NF}$ or TiCl_4

TL 24 4001 (1983)



JACS 104 4018 (1982)

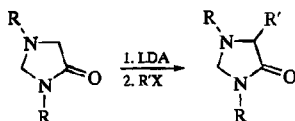
JOC 48 3631 (1983)



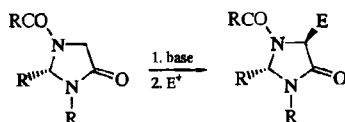
$\underline{\text{X}}$	$\underline{\text{E}^+}$	
F	RX	TL 27 6103 (1986) JOC 58 2454 (1993) (lactam) JOC 58 2454 (1993) (lactam)
	RCHO, R ₂ CO	JACS 108 4598 (1986) (chiral)
Cl	RCHO	TL 26 1343 (1985) (chiral); 27 2731 (1986) (chiral); 36 4151 (1995) JOC 55 5525 (1990) (β -lactam) TL 36 909 (1995)
OR	RX	JACS 106 8161 (1984) JOC 55 5525 (1990) (β -lactam) TL 36 4151 (1995)
	MeOCHRNHCO ₂ Me (MeO substitution) RCHO	TL 27 2731 (1986) TL 36 909 (1995)
OSiR ₃	RX MeOCHRNHCO ₂ Me (MeO substitution)	JOC 57 4765 (1992) JOC 56 2534 (1991)
SR	RX RCHO	JACS 117 8488 (1995) JACS 117 8488 (1995)
NH ₂	RX	JOC 52 4044 (1987) JACS 112 808 (1990) (inter- and intramolecular); 113 6621 (1991) (inter- and intramolec- ular)
NHR	RX	JOC 58 3473 (1993) TL 27 6361 (1986) JACS 112 808 (1990) JACS 113 6621 (1991)
NRCOR	RX	TL 31 977 (1990) (chiral, lactam)
	RX, cat Li ₂ CuCl ₄ RCHO ClCO ₂ R O ₂ (E = O ₂ H)	TL 35 2533 (1994) (chiral)

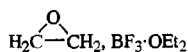


$N=CHAr$	RX	JACS 93 4324 (1971); 110 278 (1988) CC 1138 (1972) TL 375 (1972); 33 6007 (1992) Helv 51 1905 (1968) TL 31 977 (1990) CC 1138 (1972)
	$RCHO$	
	$RCOCl, ClCO_2R$	
$N=CAr_2$	$RX, ClCO_2R$	Helv 64 1145 (1981)
$N=C(SMe)_2$	RX	TL 27 3403 (1986)



JACS 111 2622 (1989)


 E^+
 RX

 Helv 68 949 (1985); 70 237 (1987)
Tetr 44 5277 (1988)
SL 515 (1991)
JOC 59 5784 (1994); 60 6408 (1995)


Tetr 44 5277 (1988)

 $RCHO$

Helv 70 237 (1987)

 $(Et_3N)_3TiCl/RCHO$

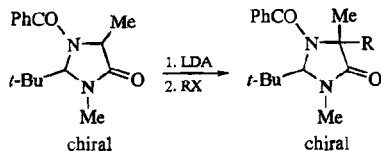
JOC 57 10 (1992); 59 3642 (1994)

 R_2CO

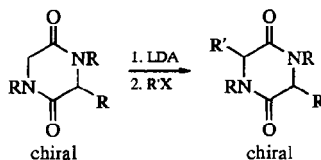
 Helv 68 949 (1985)
Tetr 44 5277 (1988)

 $CH_3CH=CHNO_2$ (1,4-addition)

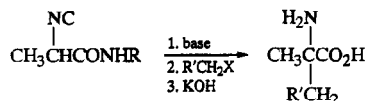
Tetr 44 5277 (1988)



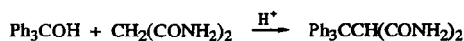
TL 32 5769 (1991)



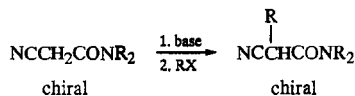
JOC 57 6532 (1992)



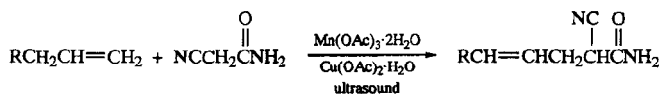
Ann 439 (1981)



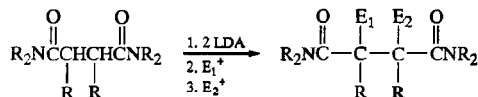
JCS 716 (1962)



TL 27 2463 (1986)

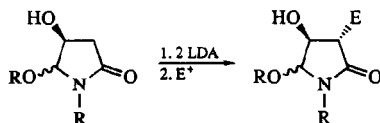


TL 35 8049 (1994)



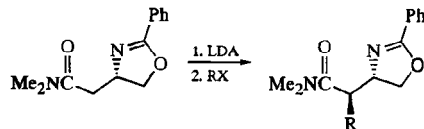
E_1^+ , E_2^+ = D_2O , D_2O ; RX , RX ; RX , RCHO ; RX , $(\text{ArSe})_2$; RX , $(\text{ArSe})_2$; $\text{Br}(\text{CH}_2)_4\text{Br}$; $\text{Br}(\text{CH}_2)_3\text{CO}_2\text{Et}$; RCO_2R , RCO_2R ; $o\text{-C}_6\text{H}_4(\text{CO}_2\text{Et})_2$; RCHO , RCHO

TL 23 3971, 3975 (1982)

 $\text{E}^+ = \text{RX}$, R_2CO^+

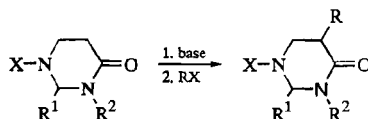
TL 28 1581 (1987)

JACS 111 2588 (1989)



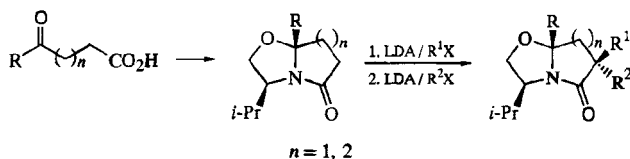
TL 24 2733 (1983)

JACS 108 4943 (1986)


 X = R, COR, CO₂R

JOC 56 2553 (1991); 58 2282 (1993); 59 7292 (1994)

TL 33 2725 (1992)



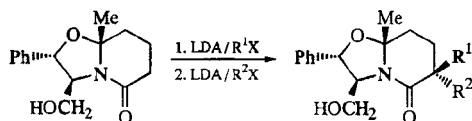
JACS 106 1146 (1984); 107 7776 (1985); 108 306 (1986); 112 8162 (1990)

TL 26 2047 (1985)

JOC 51 1541 (1986); 55 791, 3137 (1990); 58 7507 (1993); 60 6511 (1995)

Tetr 43 5663 (1987)

SL 863 (1991)

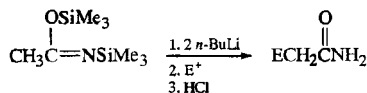


JOC 51 1936 (1986); 54 4673 (1989); 55 4233 (1990)

Tetr 43 5663 (1987)

Org Syn Coll Vol 8 241 (1993)

SL 145 (1995)


 E^+

 RCHO, R₂CO

 RCO₂R

TL 21 3227 (1980)

JACS 107 7760 (1985); 110 6180, 6186 (1988)

$\text{Me}_3\text{SiCl} / \Delta / \text{RCHO}$, $n\text{-Bu}_4\text{NF}$ or TiCl_4
 (E = CHROH)

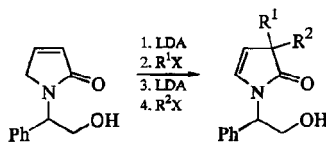
TL 27 535 (1986)

PhCO_2Me

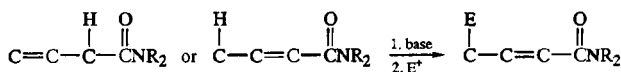
TL 1645 (1978)

PhSeBr

TL 1645 (1978)



TL 35 3931 (1994)



E^+

H_2O

JOC 50 3526 (1985)

RX

JOC 34 3263 (1969)

TL 2057 (1975)

RX , CuI

TL 1645 (1978)

JOC 46 2029 (1981)

RCHO , R_2CO

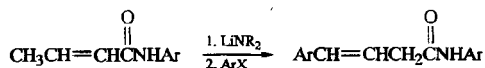
JOC 34 3263 (1969); 46 2029 (1981)

CO_2

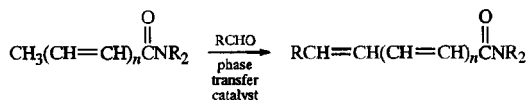
JOC 34 3263 (1969)

Me_3SiCl , Δ

TL 27 535 (1986)



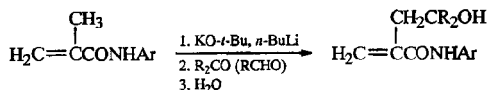
JOC 57 667 (1992)



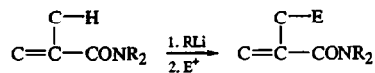
$n = 0-2$

J Chem Res (S) 106 (1981)

Ann 1725 (1981)



CL 1567 (1980)

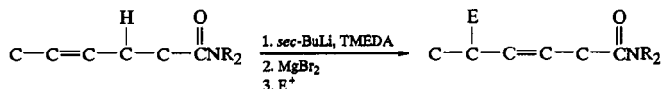


$\text{E}^+ = \text{D}_2\text{O}, \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{epoxide}, \text{RCONR}_2, \text{CO}_2, \text{H}_2\text{C}=\text{CHCONR}_2$ (1,4-addition),
 $\text{B(OMe)}_3, \text{Me}_3\text{SiCl}, (\text{PhS})_2, \text{RN}=\text{NR}$

Angew Int 13 468 (1974)

JACS 102 4550 (1980); 107 4745 (1985)

JOC 45 4257 (1980); 47 1610 (1982); 51 3921, 4627 (1986); 52 218 (1987)



$\text{E}^+ = \text{D}_2\text{O}, \text{RX}, \text{H}_2\text{CO}, \text{R}_2\text{CO}, \text{Me}_3\text{SiCl}, \text{Ph}_3\text{SnCl}$

JACS 105 6350 (1983); 109 5403 (1987)



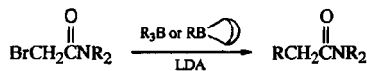
RM

RHgCl ($\text{R} = \text{aryl, vinylic}$), Li_2PdCl_4

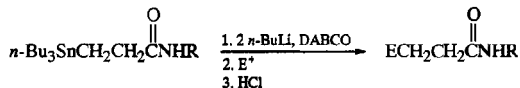
TL 30 1897 (1989)

ArI , cat Pd(OAc)_2 , NaO_2CH , LiCl or $n\text{-Bu}_4\text{NCl}$,
 $i\text{-Pr}_2\text{NEt}$

TL 34 979 (1993)



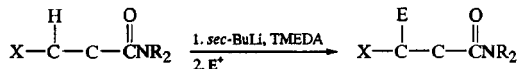
JOC 58 6118 (1993)



$\text{E}^+ = \text{MeOD}, \text{RX}, \text{R}_2\text{CO}, \text{Me}_3\text{SiCl}$

TL 23 1463 (1982)

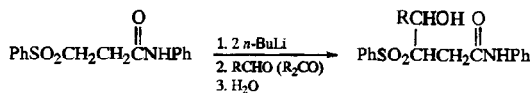
JACS 105 7182 (1983)



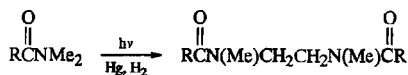
$\text{X} = \text{Ph}, \text{SPh}, \text{C}=\text{C}; \text{E}^+ = \text{D}_2\text{O}, \text{RX}, \text{R}_2\text{CO}, \text{Me}_3\text{SiCl}, \text{Ph}_3\text{SnCl}, \text{PhSSPh}$

JACS 109 5403 (1987); 115 2516 (1993) (chiral)

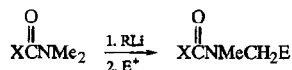
JOC 56 4938 (1991)



CL 1359 (1984)



JACS 113 2233 (1991)


 $\text{E}^+ = \text{RX, RCHO, R}_2\text{CO}$

Review: Chem Rev 78 275 (1978)

X

 2,4,6-(*i*-Pr)₃C₆H₂

TL 1839 (1977)

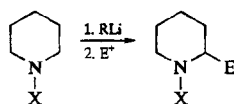
Helv 61 512 (1978)

 R₂N

Helv 61 2239 (1978)

 2,4,6-(*t*-Bu)₃C₆H₂O

Angew Int 17 274 (1978)


X
E⁺

 Me₃CCO

 RX, R₂CO, Me₃SiCl,
n-Bu₃SnCl

Tetr 39 1963 (1983)

 Et₃CCO

 MeOD, 1° RI, RCHO, R₂CO

 JOC 46 4316 (1981)
 JACS 106 1010 (1984)

 Ph₃CCO

 RX, RCHO, R₂CO

Helv 64 1337 (1981)

 2,4,6-(*i*-Pr)₃C₆H₂CO

 MeOD, RCHO, Me₃SiCl

 JOC 46 4108 (1981)
 JACS 106 1010 (1984)

MeOCO

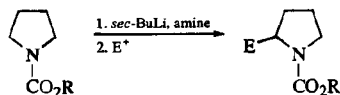
RX

 JOC 45 193 (1980) (allylic
 anion)

 PO(NMe₂)₂

 RX, RCHO, R₂CO, epoxide,
 ArH·Cr(CO)₃, I₂, Me₃SiCl,
n-Bu₃SnCl

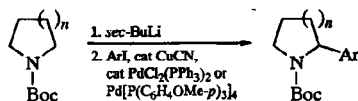
 Helv 64 643 (1981)
 Tetr 39 1963 (1983)



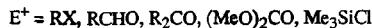
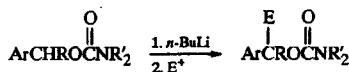
TL 30 1197 (1989); 35 829, 4067 (1994); 36 5872, 6627 (1995) (both chiral)

JOC 55 2578 (1990); 58 823, 1109 (1993); 59 274 (1994) (intramolecular); 60 8148 (1995) (chiral)

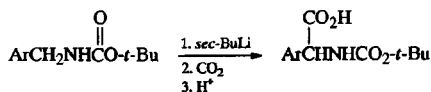
JACS 113 9708 (1991) (chiral); 115 6652 (1993); 116 3231 (1994) (chiral); 117 9369, 12342 (chiral) (1995)



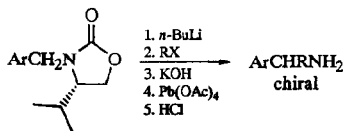
TL 36 3613 (1995)



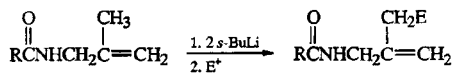
Syn 1045 (1982)



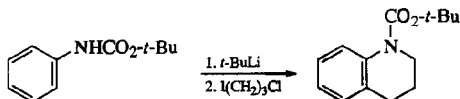
TL 34 6263 (1993)



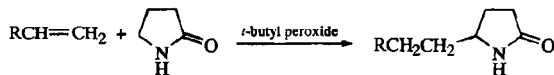
JOC 54 3002 (1989)



TL 30 2029 (1989)



TL 29 5725 (1988)



Bull Acad Sci USSR, Div Chem Sci 1745 (1964)

Proc Acad Sci USSR, Chem Sec 158 1069 (1964)



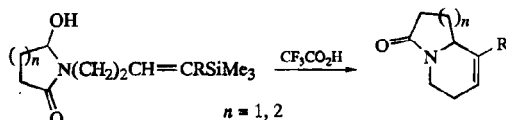
JACS 112 896 (1990)


 X = halogen, NR₂, NR₃⁺, OR, OH, O₂CR, NHCOR

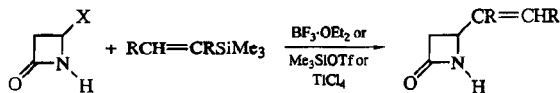
Reviews:

Org Rxs 14 52 (1965)

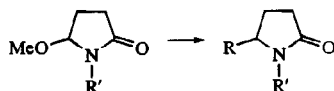
Syn 49 (1970); 85, 181 (1984)



TL 109 6097, 6115 (1987)


 X = OAc, SO₂Me

SL 885 (1991)


R

alkyl

allylic

 CH₂COR

Reagent(s)

 R₃Al

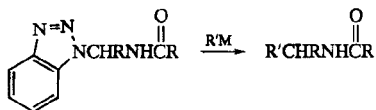
 H₂C=CHCH₂SiR₃, Lewis acid

 H₂C=CRSiMe₃, Lewis acid

JOC 46 5383 (1981)

See page 365, Section 7.

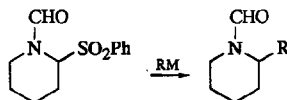
See page 1494, Section 7.2.

**R'M****RM₂X**

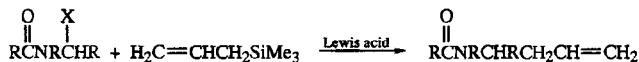
JOC 53 5854 (1988)

Et₂Zn, *n*-Bu₂NCHMeCHPhOH (chiral)

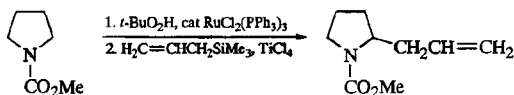
Tetr Asym 3 427 (1992)

RM = RZnX (R = aryl, vinylic, alkynyl), H₂C=CHCH₂SiMe₃ (AlCl₃),H₂C=CROSiR₃ (MgBr₂), R₂C=C(OR)OSiR₃ (AlCl₃)

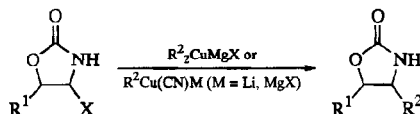
SL 48, 749 (1990)



See page 365, Section 7.

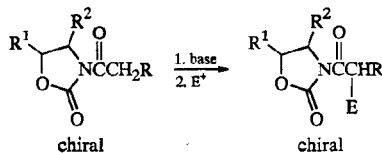


JACS 112 7820 (1990)

X = OMe, SPh; R² = 1°, 2°, 3° alkyl, aryl

TL 32 3523 (1991)

5. Imides and Related Derivatives



E^+

RX

Pure Appl Chem 53 1109 (1981)
 JACS 104 1737 (1982); 107 196 (1985); 109 1269
 (1987); 110 2506 (1988); 112 2998, 3018, 5290,
 7001, 8215 (Ti enolate) (1990); 113 2071, 5337,
 7613 (1991); 114 10653 (1992); 115 11393, 11446
 (1993)
 TL 23 807 (1982); 27 3059 (1986); 28 3651 (1987);
 29 6257 (1988); 31 1569, 5081 (1990); 32 7715
 (1991); 33 2447, 4461 (1992); 34 2229, 8163
 (1993); 36 6345 (Ti enolate), 8315 (1995)
 JOC 52 3168 (intramolecular), 3759 (1987); 53 652
 (1988); 55 6260 (1990); 56 2476 (1991); 58 2923,
 7195 (1993); 59 2261, 3347 (1994)
 SL 48 (1992); 63, 155 (1993)

 $RCHBrB(OR)_2$ [$E = CHR(OR)_2$]

JOC 59 5734 (1994)

 CF_3I , Et_3B

TL 34 2169 (1993)

 CF_2Br_2 , Et_3B ($E = CF_2Br$)

TL 36 3711 (1995)

 ICF_2CO_2R , Et_3B

TL 35 7399 (1994)

 $TfOCHRCO_2R$

JOC 60 4782 (1995)

 $RCH(OAc)C(=CH_2)CO_2R$, cat $Pd(PPh_3)_4$

TL 36 5375 (1995)

 $RC \equiv CCH(OMe)_2$, $n-Bu_2BOTf$

TL 34 2581, 2585 (1993); 36 1197 (1995) (B
 enolate)

 $[ArMn(CO)_3]BF_4$

TL 33 589 (1992)

 $AcO-C(=O)-N$, $ZnBr_2$

JACS 108 4675 (1986)

 $H_2C(OMe)_2$, $BF_3 \cdot OEt_2$

JACS 114 9434 (1992) (Ti enolate)



JACS 112 8215 (1990) (Ti enolate)

 $RCHO$, R_2CO

Li enolate

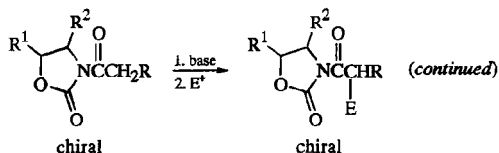
Pure Appl Chem 53 1109 (1981)
 TL 23 807 (1982); 30 5539, 5821 (1989)
 JACS 108 4595 (1986); 113 1299 (1991); 116 4674
 (1994)
 JOC 56 2489 (1991); 58 5107 (1993); 60 3000
 (1995)

Na enolate

JOC 60 3000 (1995)

K enolate

JOC 60 3000 (1995)

 E^+

B enolate

Pure Appl Chem 53 1109 (1981)
 JACS 103 2127 (1981); 107 5292 (1985); 108 4595 (1986); 110 2506, 4672, 7910 (1988); 111 1157, 7634 (1989); 112 2998, 5290, 7001, 7659 (1990); 113 1047, 7613 (1991); 114 9434 (1992); 115 522, 4497, 11446 (1993); 116 5607, 5619, 12111 (1994); 117 3448 (1995)
 TL 23 807 (1982); 24 3395 (1983); 27 3311, 5683 (1986); 28 39, 5921, 6001 (1987); 29 2247 (1988); 30 5539, 5821 (1989); 31 1443, 1731, 7587 (1990); 32 537, 931, 2453, 4905, 6645, 7288 (1991); 33 1945, 4369 (1992); 34 1851, 5343, 6783, 8147, 8167 (1993); 35 1247 (1994); 36 819, 3091, 3115, 3461, 6527 (1995)
 CC 1237 (1986)
 JOC 51 4322 (1986); 52 5588 (1987); 53 1046, 1922 (1988); 54 3487 (1989); 55 173, 2786, 6260 (1990); 56 438 (1991); 57 1067, 1070, 3493, 4331, 5059 (1992); 58 471, 1273, 3787, 5107, 5878 (1993); 59 3113, 3347, 3433 (1994); 60 4774 (1995)
 Org Syn Coll Vol 8 339 (1993)
 SL 907 (1993); 1213 (1995)

B enolate plus Lewis acid

JOC 56 5747 (1991); 60 3288 (1995)

Sn enolate

JACS 108 2476, 4595, 6757 (1986); 109 7151 (1987); 114 9434 (1992)
 TL 30 5539 (1989); 35 2659 (1994)
 JOC 57 1961, 3493, 4331 (1992); 58 5107 (1993)

Ti enolate

TL 27 897 (1986); 31 4699 (1990); 34 8293 (1993)
 JACS 113 1047, 1299 (1991)
 JOC 56 2489 (1991); 58 5107 (1993); 59 5317 (1994)

Zn enolate

JACS 108 4595 (1986)
 TL 30 5539 (1989)
 JOC 58 5107 (1993)

RCHO, ZnI_2

JACS 108 4675 (1986) (Si enolate)

RCH=NR

TL 34 1567 (1993)

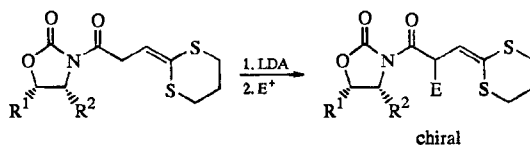
 HC(OMe)_3

JACS 112 8215 (1990) (Ti enolate)

RCOCl	JACS 106 1154 (1984) CC 1102 (1987) TL 29 2219 (1988); 32 5457 (1991) Tetr 48 2127 (1992) (Mg enolate)
(RCO) ₂ O	TL 24 4805 (1983)
H ₂ C=CHCOR (1,4-addition)	JOC 56 5750 (1991) (Ti enolate)
H ₂ C=CHCO ₂ R (1,4-addition)	JOC 56 5750 (1991) (Ti enolate); 57 1961 (1992) (Ti enolate); 60 4363, 8140 (1995) JACS 114 9434 (1992) (Ti enolate)
H ₂ C=CHCN (1,4-addition)	JACS 112 8215 (1990) (Ti enolate) JOC 56 5750 (1991) (Ti enolate)
diene-molybdenum complex	JOC 54 5141 (1989)
dienyl iron complex	JOC 54 5141 (1989)
RSO ₂ N ⁺ CHAr (E = OH)	TL 29 3459 (1988) JOC 57 1958 (1992)
(PhCH ₂ O ₂ CO) ₂ (E = OCO ₂ CH ₂ Ph)	JOC 51 3700 (1986)
RSSR	TL 35 3991 (1994)
2,4,6-(<i>i</i> -Pr) ₃ C ₆ H ₂ SO ₂ N ₃ /HOAc (E = N ₃)	JACS 109 6881 (1987); 111 1063 (1989); 112 4011 (1990); 114 1495 (1992); 115 10742 (1993) TL 31 5081 (1990); 32 2663 (1991); 33 1189, 3293 (1992); 34 953 (1993) JOC 57 1744 (1992); 59 2304, 4712 (1994); 60 4884 (1995)
TsON(Li)Boc (E = NHBoc)	TL 32 2359 (1991) (Cu enolate)
RO ₂ CN=NCO ₂ R (E = RO ₂ CNNHCO ₂ R)	JACS 108 6395, 6397 (1986) SL 615 (1995)

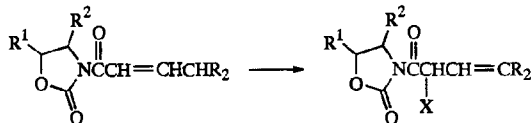
For halogenation, see page 739, Section 8.

	$\text{RCH}_2\text{C}(=\text{O})\text{X} \xrightarrow[2. \text{ reagent}]{1. \text{ LDA}} \text{XCCH(R)CH(R)C}(=\text{O})\text{X}$	
<u>X</u>	<u>Reagent</u>	
	I ₂	TL 36 4409 (1995)
	I ₂ or TiCl ₄	JOC 60 1100 (1995)
	I ₂ or Cu[O ₂ C(CH ₂) ₃ CH ₃] ₂	TL 36 4409 (1995)



$E^+ = RX, ROTf, RCHO$ (B enolate)

JOC 58 2725 (1993)



X

Reagents

R

LDA/RX

JOC 53 1046 (1988); 54 4004 (1989)

CHROH

n-Bu₂BOTf, Et₃N/RCHO

TL 27 4957, 4961 (1986); 36 1205 (1995)

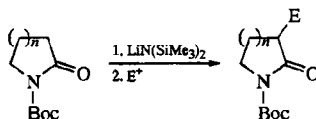
JOC 54 3009, 5708 (1989); 60 594 (1995)

JACS 112 5290 (1990)

OH

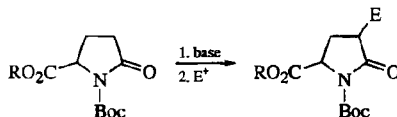
NaN(SiMe₃)₂/PhHC(=O)NSO₂Ph

JACS 107 4346 (1985)



$n = 3-5$; $E^+ = RX, (PhS)_2, PhSeCl$

SL 63 (1990)



E^+

RX

Tetr 45 7459 (1989)

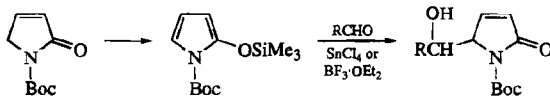
RCHO

Tetr 45 7459 (1989)

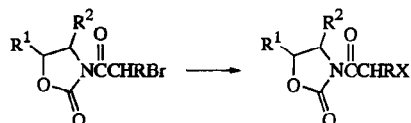
JOC 57 1920 (1992)

RCHO, BF₃·OEt₂

JOC 60 2925 (1995)



JOC 57 3760 (1992); 59 2906 (1994)

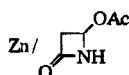


Reagents

X

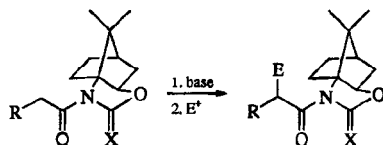


CHROH


 SnCl₂-LiAlH₄/RCHO

TL 30 5631 (1989)

TL 30 5821 (1989)



X

O

 E⁺

RX

RCHO (Li enolate)

RCHO (B enolate)

RCHO (Ti enolate)

RCHO (B enolate)

RCHO (Ti enolate)

TL 32 4959 (1991)

TL 32 5563 (1991)

TL 32 5563 (1991)

JACS 115 2613 (1993)

JOC 60 3301 (1995)

JACS 115 2613 (1993)

TL 34 3559 (1993)

JOC 60 3301 (1995)

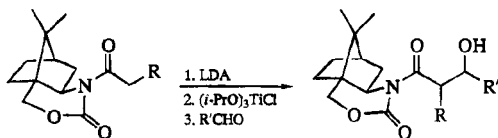
JACS 115 2613 (1993)

JOC 59 8187 (1994); 60 3301 (1995)

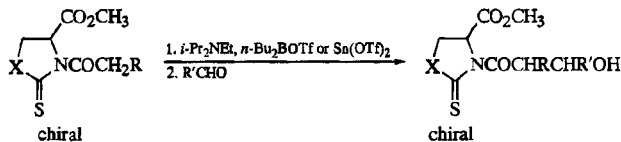
JACS 115 2613 (1993)

TL 34 3559 (1993)

JOC 60 3301 (1995)



JOC 57 5065 (1992)



X

O

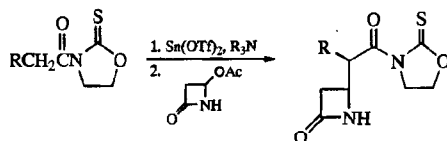
S

JOC 52 2201 (1987); 54 3988 (1989)

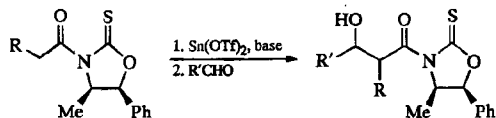
JACS 116 1753 (1994)

JOC 52 2201 (1987); 56 438 (1991)

TL 32 2577 (1991)

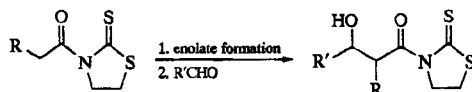


TL 27 5687 (1986)



CC 1418 (1985)

SL 38 (1990); 415 (1994)

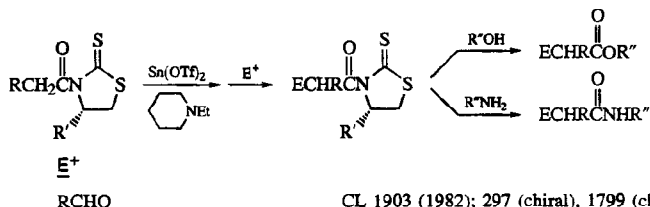
Enolate

Sn

JOC 58 471 (1993)

Ti

JOC 57 1067 (1992); 58 471 (1993)



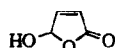
RCHO

CL 1903 (1982); 297 (chiral), 1799 (chiral) (1983)

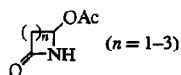
JOC 51 2391 (1986); 57 4243 (1992)

SL 42 (1989)

TL 34 8159 (1993)

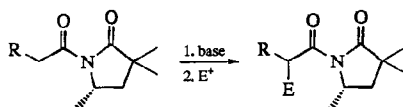


JOC 54 5211 (1989)

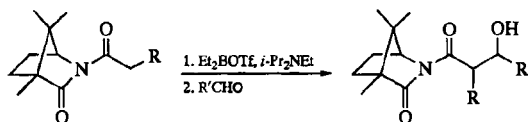


JACS 108 4673 (1986); 110 289 (1988) (both chiral)

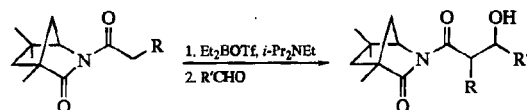
JOC 55 1148 (1990); 57 4232, 4238, 4243 (1992)

 $E^+ = RX, RCHO$

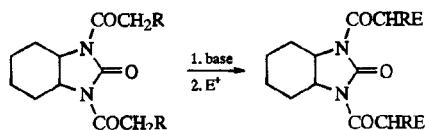
TL 35 2373 (1994)



TL 35 8521 (1994)



JACS 117 12368 (1995)

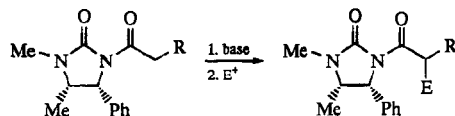

 Base/E⁺

 MN(SiMe₃)₂ (M = Na, K) / RX

TL 33 1117 (1992)

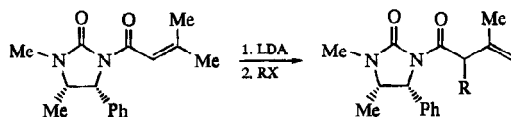
n-Bu₂BOTf, R₃N / RCHO

TL 32 4787 (1991)

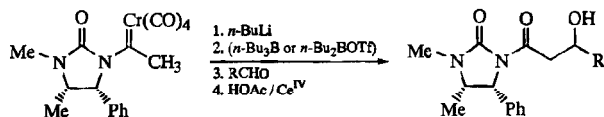

 E⁺ = RX, ArX (hv), (PhS)₂, PhSCl, PhSSO₂Ph

JOC 53 2354 (1988)

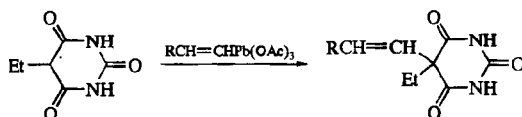
TL 33 3797 (1992); 35 7711 (1994)



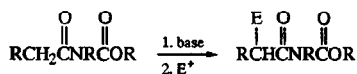
JOC 53 2354 (1988)



JOC 59 6882 (1994)



CC 965 (1984)

 E^+

RX

JOC 57 1920 (1992); 59 4327 (1994)

RCHO, R₂CO

JOC 57 1920 (1992)

TL 36 3231, 3247 (1995)

RCOCl

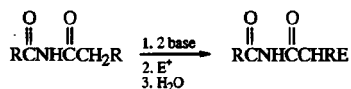
TL 27 2691 (1986)

PhSeCl

TL 33 6859 (1992)

ArSO₂N₃ (E = N₃)

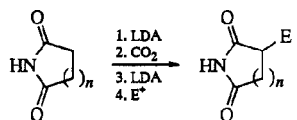
TL 33 6859 (1992)

 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCO}_2\text{R}, \text{PhSSPh}$

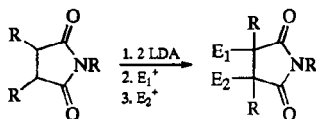
JACS 83 3468 (1961)

Can J Chem 46 2561 (1968)

JOC 51 495 (1986)

 $n = 1, 2; \text{E}^+ = \text{RX}, \text{RCOCl}, \text{RCON} \equiv \text{N}$

TL 32 4393 (1991)

 E_1^+

RX

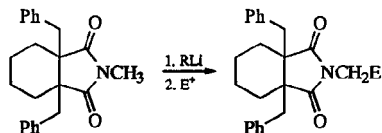
 E_2^+

RX

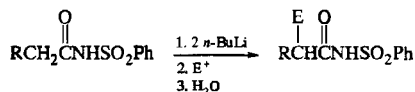
JOC 47 68 (1982)

$\text{X}-\text{C}_n-\text{X}$
(X = Br, OTs; $n = 3-5$)

JOC 47 68, 4731 (1982)

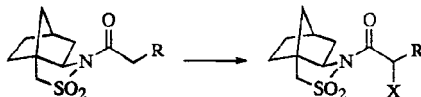
 $\text{E}^+ = \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCO}_2\text{Me}, \text{Me}_3\text{SiCl}$

Helv 60 1459 (1977)



$\text{E}^+ = \text{RX}, \text{RCH}=\text{CHCO}_2\text{R}$ (1,4-addition), I_2 (dimerization)

TL 27 131 (1986)



X

R

CH(OMe)_2

CHROH

$\text{CHRNHCO}_2\text{R}$

NHOH

Reagents

base / 1°RX

$\text{TiCl}_4, i\text{-Pr}_2\text{NEt} / \text{HC(OMe)}_3$

$\text{Et}_2\text{BOTf}, i\text{-Pr}_2\text{NEt} / \text{RCHO}$

$\text{Et}_2\text{BOTf}, i\text{-Pr}_2\text{NEt} / \text{RCHO}, \text{TiCl}_4$
 $\text{R}_3\text{SiOTf}, \text{Et}_3\text{N} / \text{RCHO}, \text{Me}_3\text{SiOTf}$
 or TiCl_4 or ZnCl_2

$\text{TiCl}_4, i\text{-Pr}_2\text{NEt} / \text{RCHO}$

$\text{LiN(SiMe}_3)_2 / \text{RCH}=\text{NCO}_2\text{R}$

$\text{NaN(SiMe}_3)_2 / \text{Cyclohexene-NO} / \text{HCl}$

TL 30 5603, 6009 (1989); 32 6547 (1991)

JACS 112 8215 (1990)

JACS 113 1047 (1991)

TL 36 4413 (1995)

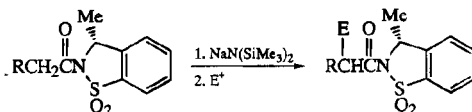
TL 34 4321 (1993)

TL 32 61 (1991); 33 2439 (1992)

JACS 113 1047 (1991)

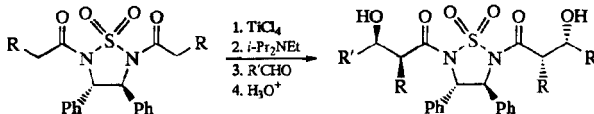
JOC 59 1238 (1994)

TL 31 991 (1990)



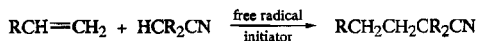
$\text{E}^+ = \text{RX}, \text{RCHO}$ (B enolate), RCOCl

TL 31 5019 (1990)

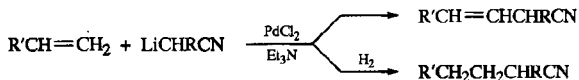


TL 33 6661 (1992)

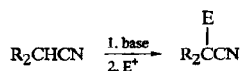
6. Nitriles



Syn 99 (1970) (review)



Organomet 1 1175 (1982)



Reviews:

Chem Rev 12 135 (1933); 20 451 (1937)

Org Rxs 9 107 (1957); 31 1 (1984)

 E^+ D_2O RX

JACS 88 2348 (1966)

J Prakt Chem (2) 39 233 (1889)

Compt Rend 182 1226 (1926)

Ann 495 84 (1932); 652 99 (1962)

JACS 67 2152 (1945); 88 2348 (1966); 115 3030

(1993); 116 1753, 2621 (1994)

BSCF 1881 (1965)

Tetr 24 175 (1968); 31 153 (1975); 36 775 (1980)

TL 707 (1974); 27 3685 (1986); 28 4329 (1987); 30

1499 (1989); 33 6683 (1992); 36 8299 (1995)

(intramolecular)

J Polym Sci, Polym Chem Ed 17 3499 (1979)

JOMC 204 281 (1981)

JOC 46 4600 (1981); 51 3007, 4080 (intramolecular)

(1986); 52 4142 (1987); 53 477 (1988); 54 1439,

3422 (1989); 56 550 (1991); 57 2732 (1992); 59

6464 (1994); 60 5537 (1995)

Syn 305 (1982)

Can J Chem 61 2006 (1983)

CC 279 (1986); 1342 (1987)

 ArX

JOC 48 4397 (1983); 50 1334 (1985); 51 5157

(1986); 52 1333, 2619 (1987); 55 1471, 4817,

4822 (1990); 58 7115 (1993)

 $\text{ArX} \cdot \text{Cr}(\text{CO})_3$ [$\text{E} = \text{Ar} \cdot \text{Cr}(\text{CO})_3$]JACS 96 7091 ($\text{X} = \text{F}, \text{Cl}$), 7092 ($\text{X} = \text{Cl}$) (1974)TL 29 1135 (1988) ($\text{X} = \text{OMe}$); 36 5511 (1996)($\text{X} = \text{OMe}$) $p\text{-(NO}_2)_2\text{C}_6\text{H}_4$ ($\text{E} = p\text{-NO}_2\text{C}_6\text{H}_4$)

CL 31 (1986)

 $p\text{-NO}_2\text{C}_6\text{H}_4\text{CHO}$ ($\text{E} = p\text{-NO}_2\text{C}_6\text{H}_4$)

CL 173 (1986)



epoxide

JOC 59 520 (1994)

JOC 51 2230 (1986)

TL 29 277 (1988); 32 939 (1991); 33 6683 (1992)

SL 889 (1992)

 $\text{RCHO}, \text{R}_2\text{CO}$


JOMC 9 125 (1967); 57 C36 (1973)

Ber 101 3113 (1968)

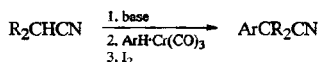
JOC 33 3402 (1968); 53 2394 (1988); 54 3422, 3800

(1989); 59 4053 (1994); 60 2261 (1995)

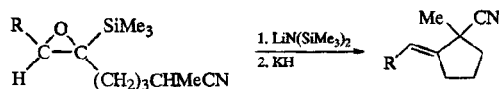
Gazz Chim Ital 103 117 (1973)

	Coll Czech Chem Commun 46 1682 (1981) Tetr 37 4111 (1981) (chiral ligand) Syn 297 (1983) JACS 108 1311 (1986); 109 613 (1987); 114 5445 (1992); 115 3146 (1993) TL 28 1611 (1987); 30 5937 (1989); 35 1339, 3935 (1994)
RCH=NSiR ₃	JOC 54 3422 (1989)
RCO ₂ R	JACS 54 2960 (1932); 67 2152 (1945); 69 990 (1947); 79 725, 728 (1975); 111 643 (1989) (lactone) TL 24 2059 (1983); 28 4641, 4645 (1987) (both intramolecular); 29 4285 (1988) JOC 59 4040 (1994)
RCO ₂ CO ₂ Et	TL 1585 (1979)
RCON(Me)OMe	JOC 54 4229 (1989)
	SL 139 (1993)
CO ₂	JOC 31 3873 (1966)
EtOCO ₂ Et	JOC 58 6596 (1993)
RCN	JOMC 9 125 (1967) TL 24 3509 (1983)
Me ₃ SiCl	JOMC 9 125 (1967)

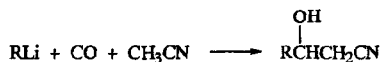
For halogenation, see page 739, Section 9.



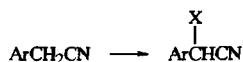
JACS 97 1247 (1975); 98 6387 (1976); 99 959 (intramolecular), 1675 (1977); 101 217, 3535 (1979)
 JOC 44 3275 (1979) (inter- and intramolecular); 55 2073 (1988)
 Tetr 37 3957 (1981)
 Pure Appl Chem 53 2379 (1981) (review)
 JOMC 221 147 (1981); 226 183 (1982); 240 C5 (1982)
 CC 1359 (1982)
 Organomet 2 467 (1983)
 TL 34 1399 (1993)



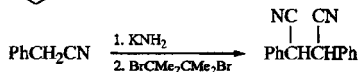
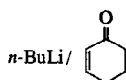
JOC 54 2043 (1989)



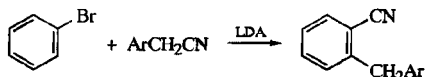
JOC 60 5973 (1995)



<u>X</u>	<u>Reagents</u>	
R	Na, ROH	TL 1509 (1966) Chem Pharm Bull 15 1811 (1967); 18 550 (1970) JOC 36 2948 (1971) TL 32 7195 (1991) TL 22 4107 (1981)
	ROH, EtO ₂ CN=NCO ₂ Et, PPh ₃ 1° ROH, cat RhCl ₃ ·3H ₂ O-PPh ₃ - Na ₂ CO ₃ or cat H ₂ Ru(PPh ₃) ₄ NaOH, RX, cat (PhCH ₂ NEt ₃)Cl	Rocz Chem 39 1223, 1401, 1595, 1805 (1965); 40 1647, 1839 (1966); 41 1037, 1303 (1967); 43 79 (1969) Org Syn Coll Vol 6 897 (1988) Org Syn Coll Vol 3 219 (1955) JOC 60 5795 (1995) J Med Chem 21 548 (1978) SL 723 (1992)
	NaNH ₂ , RX LiN(SiMe ₃) ₂ /RX LDA/RX	Syn Commun 13 35 (1983)
CH ₂ CR=CHR	n-BuLi / RO ₃ SPh	SL 597 (1993)
CR ₂ COR	BrCH ₂ CR=CHR, K ₂ CO ₃ , n-Bu ₄ NI	JOC 60 5419 (1995)
CR ₂ CN	base / BrCR ₂ COR	JOC 60 5419 (1995)
o- or p-ArNO ₂	base / BrCR ₂ CN	TL 673 (1969)
	o- or p-ClArNO ₂ , NaOH, cat (PhCH ₂ NEt ₃)Cl	Org Syn Coll Vol 6 940 (1988)
CH=CH ₂	HC≡CH, KOH, cat (PhCH ₂ NEt ₃)Cl	SL 639 (1991)
C≡CH	H ₂ C=CCl ₂ , NaOH, cat (n-Bu ₄ N)HSO ₄	JOC 60 7511 (1995)
CHROH	LDA / RCHO	JOC 36 2948 (1971)
COR	Na, RCO ₂ R	J Med Chem 21 548 (1978)
CO ₂ H	LDA / CO ₂ / H ₃ O ⁺	Tetr 37 1927 (1981)

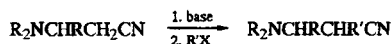


JOC 35 2085 (1970)

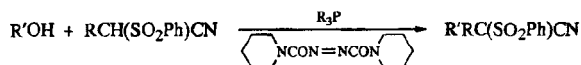


TL 25 2941 (1984)
JOC 53 4915 (1988); 55 1471 (1990)
JACS 110 7178 (1988)

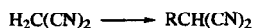
		$\text{XCHRCN} \xrightarrow[2. \text{E}^+]{1. \text{base}} \begin{array}{c} \text{E} \\ \\ \text{XCRCN} \end{array}$
<u>X</u>	<u>E⁺</u>	
OR	RX	JOC 55 5550 (1990); 57 1559, 4793 (1992) IACS 114 8375 (1992); 117 197 (1995) TL 35 7601 (1994)
SR	RX	Syn Commun 3 265 (1973)
NR ₂	RX	TL 28 547 (1987); 29 631, 1391 (1988); 32 2485, 2489 (1991); 36 2991 (1995) SL 747, 878 (1991) JOC 57 4211 (1992); 58 6451 (1993) JOC 52 2427 (1987)
	R ₂ CO	
N=CHAr	RX	SL 161 (1990) (intramolecular)
NRCOR	ROMs	TL 33 4889 (1992) (intramolecular)
CO ₂ R	—	See page 1724, Section 2.
CONR ₂	—	See page 1778, Section 4.



TL 35 8769 (1994)



TL 36 5691 (1995)


 3° RCl(Br), AlCl₃

 Naturwiss 51 288 (1964)
Angew Int 5 1044 (1966)
Org Syn Coll Vol 6 223 (1988)

Na base / ArCH=CHCHRCI, hv

Austral J Chem 36 527 (1993)

 KO-*t*-Bu / BrCR₂COR

JOC 60 5419 (1995)

 NaH / ArI, cat Pd(PPh₃)₄

 CC 932 (1984)
JOC 59 3077 (1994)

 ArI, cat CuI, K₂CO₃, DMSO

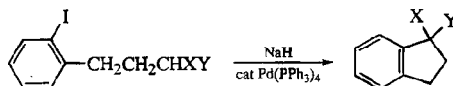
JOC 58 7606 (1993)

 1° ROH, EtO₂CN=NCO₂Et, PPh₃

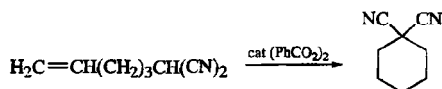
TL 1279 (1972)

 Ph₃COH, Δ

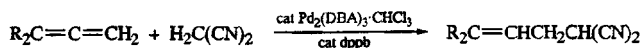
JCS 716 (1962)


 X, Y = CO₂R, CN; CN, CN

JOC 53 4149 (1988)

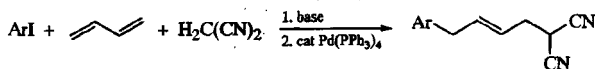


BSCF 2415, 2427 (1969)



JACS 116 6019 (1994)

TL 35 2811 (1995)

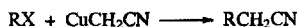


JCS Perkin I 647 (1990)



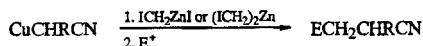
CL 1511 (1984) (RX = aryl bromide)

JACS 109 7223 (1987) (RX = heterocyclic iodide)



TL 487 (1972)

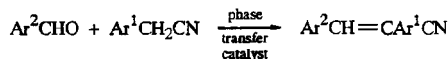
JOC 53 1616 (1988)

E⁺ = allylic bromide, enone (1,4-addition)

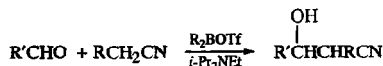
JOC 58 2694 (1993)



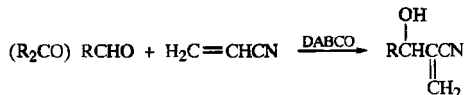
TL 35 1177 (1994)



Syn 913 (1981)



CL 1401 (1982)

TL 27 4307, 5007 (1986); 28 4351 (1987) (RCOCO₂R); 34 7049 (1993); 35 7947 (1994)

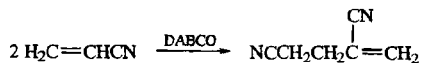
Syn Commun 17 587 (1987)

Tetr 44 4653 (1988) (review)

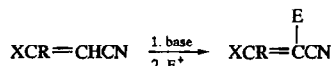
J Chem Res (S) 330 (1988) (high pressure)

Tetr Asym 2 969 (1991) (chiral)

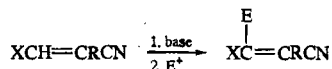
SL 444 (1994) (microwave)



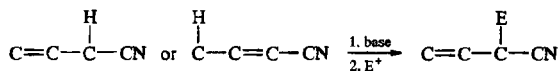
TL 28 4591 (1987)


 $\text{X} = \text{Ar, OR, NR}_2, \text{SR}$

See page 351, Section 1.


 $\text{X} = \text{OR, NR}_2$

See page 351, Section 1.


 E^+

RX

BSCF 951 (1965)

JOC 36 877 (1971); 40 1162 (1975); 44 300 (1979);

54 1876 (1989)

TL 1377 (1974); 4647 (1975); 35 7601 (1994)

Tetr 31 153 (1975)

RCHO

JACS 111 643 (1989)

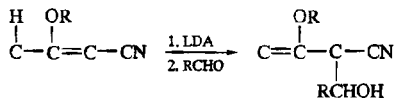
 $\text{RCH}=\text{CHCO}_2\text{R}$ (1,4-addition)

CL 1085 (1986)

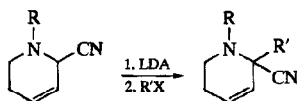
TL 28 1785 (1987)

 $\text{H}_2\text{C}=\text{CHCN}$ (1,4-addition)

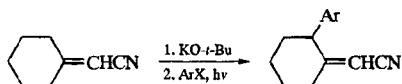
JACS 65 18 (1943)



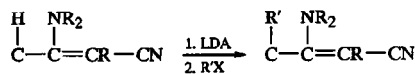
JACS 111 643 (1989)



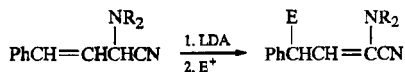
TL 28 6179 (1987)



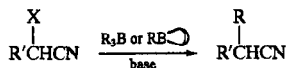
JOC 53 6065 (1988)



TL 3963 (1974)

 $\text{E}^+ = \text{RX}, \text{RCHO}$

JOC 58 1754 (1993)

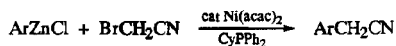
 $\text{X} = \text{Cl}, \text{Br}; \text{R}' = \text{H}, \text{Cl}, \text{alkyl}, \text{CO}_2\text{R}; \text{R} = \text{alkyl}, \text{vinyl}$

JACS 91 6854 (1969); 92 5790 (1970); 111 1754 (1989)

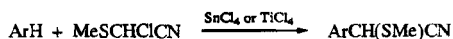
Organomet Chem Syn 1 95 (1970)

JOC 46 229 (1981); 51 3398 (1986) ($\text{R} = \text{vinyl}$); 57 2732 (1992)

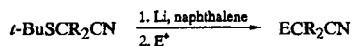
TL 23 2077 (1982)



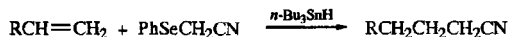
Syn 40 (1987)



Chem Pharm Bull 30 3574 (1982)

 $\text{E}^+ = \text{H}_2\text{O}, \text{RX}, \text{RCHO}, \text{R}_2\text{CO}, \text{RCOCl}, \text{HCO}_2\text{R}$

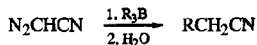
Syn Commun 3 265 (1973)



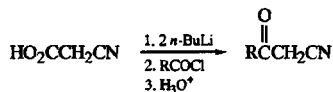
TL 31 227 (1990)



TL 33 6953 (1992)



JACS 90 6891 (1968)



Syn 308 (1983)

6. CONJUGATE ADDITION TO α,β -UNSATURATED NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES

Reviews:

Org Prep Proc Int 2/ 705 (1989) (organolithium compounds)

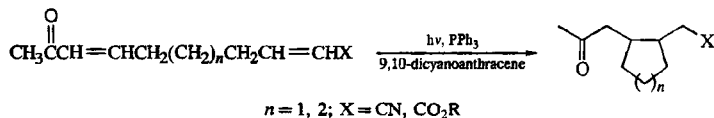
Org Rxs 38 225 (1990) (β -addition followed by α -functionalization)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Parts 1.1-1.6

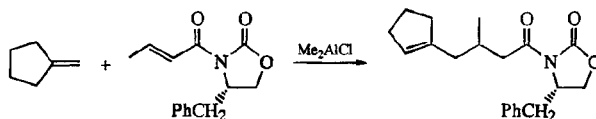
P. Perlmutter, "Conjugate Addition Reactions in Organic Synthesis," Tetrahedron Organic Chemistry Series, Vol 9, Pergamon, New York (1992)

Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21b, G. Thieme, Stuttgart-New York (1995), pp 2041-2156 (enantioselective)

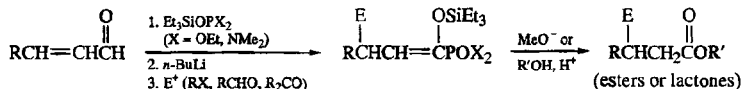
For conjugate additions to α,β -unsaturated keto amides, see page 1599, Section 18 and page 1614, Section 20, and for nitroalkenes, see page 1511, Section 12.



See page 77, Section 1.



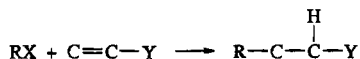
JOC 56 4908 (1991)



TL 2047 (1979)

JACS 101 371 (1979)

BCSJ 55 224 (1982)



Reviews:

Angew Int 22 753 (1983); 24 553 (1985)

Chimia 39 203 (1985)

Chem Rev 88 487 (1988) (organomercurials)

Acct Chem Res 24 296 (1991)



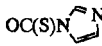
"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 4, Part 4.1, p 715

SL 1 (1994) (diastereofacial selection)

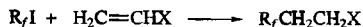
Houben-Weyl, "Methods of Organic Chemistry," 4th ed, Vol E21c, G. Thieme, Stuttgart-New York (1995), pp 2203-2287 (enantioselective)

<u>Y</u>	<u>X</u>	<u>Reagent(s)</u>	
CO ₂ H	halogen	<i>n</i> -Bu ₃ SnH NaBH ₄ , (HO) _n Sn(CH ₂ CH ₂ CO ₂ K) ₂ , [HO ₂ CCH ₂ CH ₂ C(Me)- (CN)N=I ₂	CC 944 (1983) TL 35 6221 (1994) (intramolecular)
CO ₂ R	halogen	Li (Me ₃ Si) ₃ SiH <i>n</i> -Bu ₃ SnH	TL 30 5563 (1989) JOC 59 5317 (1994) (intramolecular) JOC 47 3348 (1982); 48 1782 (1983) (intramolecular); 50 546 (1985) (intra- molecular); 54 2268 (1989) (intra- molecular); 55 6028 (1990) (intra- molecular, R = aryl); 57 573 (intra- molecular, 752 (intramolecular, R = aryl), 2625 (intramolecular) (1992), 58 4293 (1993) (intra- molecular); 59 5128 (intramolecular, lactone), 5317 (intramolecular), 6136 (1994) TL 27 5071 (1986) (intramolecular, R = vinyl); 28 5853 (1987); 29 1375, 3869 (intramolecular), 4685 (intra- molecular, R = aryl, lactone), 4963 (intramolecular) (1988); 30 743, 2829 (intramolecular) (1989); 32 3469 (intramolecular), 7587 (1991); 33 1945 (intramolecular, R = vinyl), 6719 (intramolecular) (1992); 34 4831 (intramolecular), 5251 (intramolec- ular, propargylic → allenic), 7053 (1993); 35 2837, 3995, 4823 (lactone), 6361 (1994) (all intramolecular); 36 417 (intramolecular), 4047 (1995) JACS 108 3102 (1986) (intramolecular); 109 4976 (1987) (intramolecular); 112 6740 (1990); 115 11744 (1993) (intramolecular, R = aryl); 117 8017 (1995) (intramolecular)

			Angew Int 25 450 (1986) CC 1006, 1438 (intramolecular) (1987) Ann 231 (1987) CL 2417 (1987) SL 575 (1990) (intramolecular, R = allylic); 165 (intramolecular), 423, 425 (1991); 607, 918 (intra- molecular, lactone) (1995)
		<i>n</i> -Bu ₃ SnH, Et ₃ B, Lewis acid	JOC 60 3576 (1995) TL 36 269 (1995) (intramolecular, R = vinylic)
		<i>n</i> -Bu ₃ SnCl, NaBH ₃ CN Ph ₃ SnH (<i>n</i> -Bu ₃ Sn) ₂ , 1,4-dihydro- benzene, <i>i</i> -PrOH, <i>hν</i> cat Pd(PPh ₃) ₄ vitamin B ₁₂ , photoelectro- catalysis Zn, cat vitamin B ₁₂ , Et ₃ N	TL 33 3907 (1992) (intramolecular) CC 944 (1983) SL 287 (1993) TL 28 3179 (1987) (R = Ar) TL 29 1601 (1988) Helv 75 638 (1992) SL 201 (1995) Helv 75 638 (1992) TL 29 351 (1988); 33 5261 (1992) (intramolecular) TL 33 5261 (1992) (intramolecular); 36 417 (1995) (intramolecular) JOC 54 279 (1989) (intramolecular) JOC 47 3348 (1982) TL 28 5853 (1987) CC 944 (1983) TL 30 1209 (1989) TL 30 1209 (1989)
	OC(S)SMe	Zn, ultrasound, H ₂ O <i>n</i> -Bu ₃ SnH	
	OC(S)N $\begin{array}{c} \diagup \\ \diagdown \end{array}$ N	<i>n</i> -Bu ₃ SnH	
	SPh	<i>n</i> -Bu ₃ SnH	
	SePh	<i>n</i> -Bu ₃ SnH	
	TeAr	Ph ₃ SnH	
	TeCl ₂ Ar	<i>n</i> -Bu ₃ SnH	
CO ₂ R, CN	halogen	(Me ₃ Si) ₃ SiH, AIBN <i>n</i> -Bu ₃ SnH	TL 30 681 (1989) Angew Int 23 69 (1984) Israel J Chem 26 387 (1985) JOC 52 3659 (1987); 53 1285, 1432 (1988); 58 2509 (1993) (sequential) TL 29 2335, 4133 (1988); 31 4341 (1990) (R = vinylic); 32 6097 (1991); 34 3087 (1993) Angew Int 23 69 (1984) JOC 51 3726 (1986) TL 34 7819 (1993) TL 30 2907 (1989) Pure Appl Chem 55 1791 (1983); 59 363 (1987) JOC 60 7684 (1995)
		cat <i>n</i> -Bu ₃ SnCl, NaBH ₄ , <i>hν</i> (<i>n</i> -Bu ₃ SnOCPh ₂) ₂ [CpFe(CO) ₂] ₂ , <i>hν</i> vitamin B ₁₂ , reductant	
		cat NiBr ₂ , py, electrolysis (R = aryl) cat NiCl ₂ ·6H ₂ O, Zn, py (R = 1°, 2°, 3° alkyl; aryl; vinylic) Zn, FeCl ₃ , NaI, py (Me ₃ Si) ₃ SiH, AIBN	TL 30 689 (1989) JOC 60 6574 (1995) JOC 58 6517 (1993) TL 31 6013 (1990)
	—N≡C		

<u>Y</u>	<u>X</u>	<u>Reagent(s)</u>	
	NHNH ₂	CuSO ₄ (R = Ar)	TL 30 4709 (1989)
	NO ₂	<i>n</i> -Bu ₃ SnH	CL 635 (1985)
	OC(S)SMe	cat <i>n</i> -Bu ₃ SnCl, NaBH ₄ , hv	Angew Int 23 69 (1984)
CO ₂ R, CN, CONH ₂	I	Zn, CuI, THF, H ₂ O	TL 33 3319, 8069 (1992); 35 3301 (1994)
CO ₂ R, CONR ₂ , CN	halogen	Zn, CuI, EtOH, H ₂ O, ultrasound	JOC 58 118 (1992) TL 35 275 (1994)
CONR ₂	halogen	<i>n</i> -Bu ₃ SnH	TL 28 5853 (1987); 34 2445 (1993); 35 4031 (1994) (intramolecular)
		<i>n</i> -Bu ₃ SnH, Et ₃ B, Lewis acid	JACS 111 8311 (1989); 112 6740 (1990); 113 1791 (1991)
		Ph ₃ SnH	SL 384 (1990) (intramolecular, R = aryl)
			JOC 60 3576 (1995)
			TL 30 2585 (1989) (intramolecular, R = aryl)
			TL 36 625 (1995) (intramolecular)
	SePh	<i>n</i> -Bu ₃ SnH	
		<i>n</i> -Bu ₃ SnH, hv	TL 31 1679 (1990)
CONRCOR	halogen	<i>n</i> -Bu ₃ SnH	JACS 113 5918 (1991); 114 7007 (1992) (chiral)
	halogen	<i>n</i> -Bu ₃ SnH, Lewis acid, Et ₃ B, O ₂	JACS 117 10779 (1995)
CN	halogen	(Me ₃ Si) ₃ SiH <i>n</i> -Bu ₃ SnH	JOC 56 678 (1991) Angew Int 22 622 (1983) CC 1006 (1987) Org Syn 65 236 (1987) TL 31 2975 (1990) (intramolecular)
			JOC 55 5442 (1990); 57 3365 (1992); 58 3100 (intramolecular; R = alkyl, vinyl, aryl); 3483 (1993); 60 3871 (1995) (serial cyclization)
			JACS 114 4067 (1992) Org Syn Coll Vol 8 148 (1993)
		vitamin B ₁₂ , reductant	Chimia 39 211 (1985)
		electrolysis (R = Ar)	JOC 56 586 (1991)
	NO ₂	<i>n</i> -Bu ₃ SnH	JACS 107 4332 (1985) JOC 58 898, 3483 (1993)
	OC(S)SMe	(Me ₃ Si) ₃ SiH <i>n</i> -Bu ₃ SnH	JOC 56 678 (1991) Angew Int 23 69 (1984)
	OC(S)N 	<i>n</i> -Bu ₃ SnH	Angew Int 23 69 (1984) TL 28 4645 (1987)
	SePh	(Me ₃ Si) ₃ SiH <i>n</i> -Bu ₃ SnH	JOC 54 109 (1989) JOC 56 678 (1991) SL 555 (1995)

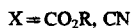
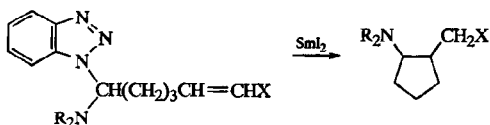
	$\text{—N}\equiv\text{C}$	$(\text{Me}_3\text{Si})_3\text{SiH}$	JOC 56 678 (1991)
OAc	halogen	$n\text{—Bu}_3\text{SnH}$	JOC 52 3659 (1987)



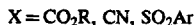
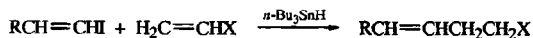
X

Reagents

CO ₂ R	Zn, cat bromo(py)cobaloxime	TL 32 4001 (1991)
	Zn, cat MCl ₃ (M = Sm, Dy, Y)	JOC 57 3339 (1992)
		TL 33 8119 (1992)
CN	Zn, cat bromo(py)cobaloxime	JOC 57 3339 (1992)

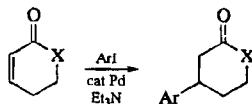


TL 34 549 (1993)



TL 35 9605 (1994)

SL 1045 (1995) (intramolecular, plus R₃Al or MAD, X = CO₂R)



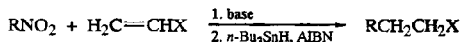
X

O

TL 28 3179 (1987)

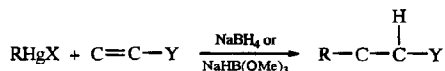
NR

JACS 114 1800 (1992)



R = 2° alkyl, 1° allylic or benzylic; X = CN, CO₂R, SPh, SO₂Ph, CHO, COR

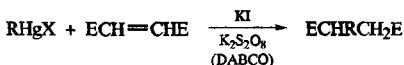
JOC 50 3692 (1985); 52 1601 (1987) (KF-alumina as base, no reduction)



Y = CO₂R, CO₂COR, CONR₂, CONRCOR, CN

R = 1°, 2°, 3° alkyl; benzyl; MeO—C—C—; MeO—C—C—C—; C=C—C(OMe)—C—; HCO—C—C—; RCOCHRCH₂; RCONR—C—C—

Ber 110 2588 (1977); 112 3759, 3766 (1979); 113 1192, 2787 (1980); 114 1572 (1981); 115 2526 (1982); 117 859, 2132, 3160, 3175 (1984); 118 1289, 1345, 1616 (1985); 119 1291 (1986)
 TL 2779, 2783 (1977); 21 1829, 3569 (1980); 22 2155 (1981); 23 931, 2765 (1982); 24 11, 15, 2051, 3221 (1983); 25 2743 (1984); 27 4841 (1986); 32 707 (1991); 34 2445, 4489, 7053 (1993); 36 4295, 7639 (1995)
 Angew Int 18 154 (1979); 20 965 (1981); 21 130 (1982); 24 553 (1985) (review); 26 479 (1987)
 JOC 47 3348 (1982); 49 1313 (1984)
 Syn 735 (1982)
 Organomet 1 675 (1985)
 Tetr 41 4025 (1985)
 JACS 111 8311 (1989); 112 6741 (1990); 113 1791, 5918 (1991); 114 7007 (1992); 116 3131 (1994)
 SL 423 (1991)



E = CO₂R, CONR₂; R = 3° > 2° > 1° alkyl

SL 87 (1990)
 TL 31 6273 (1990)
 JACS 117 3952 (1995)

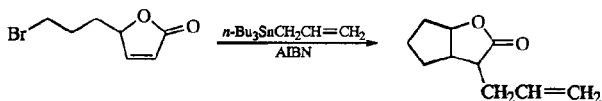


X

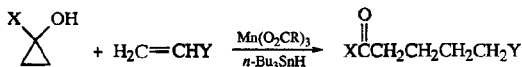
CO₂R

CN

TL 35 3841 (1994)
 JACS 117 3952 (1995)
 JACS 117 3952 (1995)

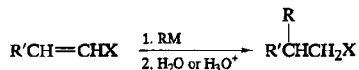


SL 918 (1995)




X = R, OR, NR₂; Y = CO₂R, CN, CONR₂

BCSJ 66 819 (1993)

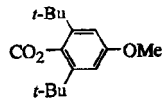

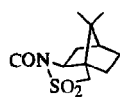


Reviews:

Org Rxns 10 179 (1959) (Michael addition); 19 1 (1972) (organocopper reagents); 41 135 (1992) (organocopper reagents)
 Chem Rev 92 771 (1992) (asymmetric)

<u>X</u>	<u>RM</u>	
CO ₂ H	RLi	JOC 52 5729 (1987)
	RMgX	JACS 75 6342 (1953) BSCF II 116 (1982) JOC 52 5729 (1987) JACS 100 3240 (1978) JOC 47 119 (1982)
	RCu·BF ₃	
CO ₂ R'	RLi (R = 1° alkyl, vinylic)	SL 613 (1990)
	RLi, MAD	JACS 110 3588 (1988)
	R ₃ SnLi	JACS 99 4836 (1977)
	RMgX	BCSJ 39 910 (1966) Org Syn Coll Vol 5 762 (1973)
	RMgX, cat CuX	JOC 27 2706 (1962); 42 3209 (1977); 45 4117 (1980) BCSJ 39 910 (1966) Syn Commun 9 325 (1979) CC 1472 (1987) JACS 110 4763 (1988); 116 8126 (1994) TL 31 7623 (1990) (lactone) JOC 59 1946 (1994) TL 31 1161 (1990)
	RMgX, cat CuI, Me ₃ SiCl	
	RMgX, cat Cu(I) or Cu(II), Me ₃ SiCl, (HMPA)	
	RMgX, cat CuCl, Me ₃ SiCl	TL 31 7425 (1990)
	RMgX, cat CuX ₂ , Me ₃ SiCl	TL 31 7457 (1990)
	RMgBr, cat CuBr·SMe ₂ , Me ₃ SiCl, HMPA	TL 27 4025 (1986)
	RMgX, cat CuI, cat	TL 36 4275 (1995)
	 (chiral) CONMe ₂	
	R ₂ CuMgX	JOMC 199 9 (1980) TL 28 3791 (1987)
	R ₂ CuMgX, Me ₃ SiCl	TL 31 1011 (1990)
	R ₂ CuLi	JACS 94 5495 (1972); 103 1222 (1981); 110 4763 (1988); 111 2984 (1989); 114 7652 (1992) (R = vinyl, meth- allyl); 116 3312 (1994) JOC 38 3893 (1973); 46 3874 (1981); 51 3376, 5041 (1986); 52 3541 (2- alkylidene-4-alkanolide), 4603 (2- alken-4-olide) (1987); 53 1600 (1988); 57 4300 (1992) CC 907 (1973) Acta Chem Scand B 31 667 (1977); 34 113 (1980) Syn Commun 9 325 (1979) Tetr 37 3981 (1981) TL 27 2519 (1986) (2-alken-4-olide); 28 949 (2-alken-4-olide), 3791 (2-alkyl- idene-5-alkanolide) (1987); 29 4411 (1988); 31 7623 (1990) (2-alken-5- olide); 33 5689 (1992) (2-alken-4- olide)

<u>X</u>	<u>RM</u>	
	$(H_2C=CR)_2CuLi$, (Me_3SiCl)	JOC 57 2960 (1992)
	$(2-py)_2CuLi$, LiI	Tetr 38 1509 (1982)
	R_2CuLi , Me_3SiCl	TL 27 1047 (1986); 31 345, 1011 (1990)
		JOC 51 5041 (1986); 54 3963 (1989)
	$RCu(Ar)Li$	Acta Chem Scand B 31 667 (1977); 32 483 (1978)
		Tetr 34 3023 (1978)
	$2-pyCu(Ph)Li$, LiI	Tetr 38 1509 (1982)
	$[RCuC\equiv C(CH_2)_2CH_3]Li$	TL 28 3551 (1987) (R = vinylic)
		JACS 111 2737 (1989) (R = alkyl); 113 9682 (1991) (R = vinylic)
	RLi , $CuC\equiv CSiMe_3$, Me_3SiCl	TL 28 5719 (1987)
	$RCu(CN)Li$	TL 22 2985 (1981)
		JACS 115 3146 (1993)
	$R_2Cu(CN)Li_2$	TL 24 127 (1983); 29 3911 (1988); 33 5689 (1992) (2-alken-4-olide)
	$(H_2C=CH)_2Cu(CN)Li_2$	JACS 109 7495 (1987); 114 7652 (1992)
	$(H_2C=CH)_2Cu(CN)Li_2$, $BF_3 \cdot OEt_2$	JACS 114 7652 (1992)
	$ThCuR(CN)Li_2$	JOMC 285 437 (1985)
		JACS 114 2260 (1992); 115 4497 (1993) (both R = vinylic)
	$ThCu(CH=CHR)(CN)Li_2$, $BF_3 \cdot OEt_2$	JACS 112 8465 (1990)
	RCu	JACS 114 7652 (1992) (R = methallyl)
	$RCu \cdot BF_3$	JACS 100 3240 (1978); 109 5820 (1987); 114 7652 (1992); 115 10139 (1993)
		Helv 64 2808 (1981)
		JOC 47 119 (1982)
		CC 904 (1984); 464, 1572 (1987)
	$PhCH_2Cu$, Me_3SiCl , TMEDA	TL 27 943 (1986)
	RCu , Me_3SiI	TL 33 2383 (1992)
	RLi , $n-Bu_3P \cdot CuI$	JOC 58 7238 (1993)
	$RCu \cdot n-Bu_3P \cdot BF_3$	TL 27 4713 (1986)
		TL 24 4971 (1983); 27 1139 (1986); 35 7455 (1994)
		Helv 68 212 (1985)
	R_2CuLi , $BF_3 \cdot OEt_2$	Tetr 37 3981 (1981)
		JACS 104 1774 (1982); 109 5820 (1987); 111 1351 (1989); 114 7652 (1992) (R = vinyl); 115 10139 (1993)
		CC 1572 (1987)
	R_2CuLi , 2 $BF_3 \cdot OEt_2$	JACS 115 10139 (1993)
		JOC 58 4346 (1993)
	R_3CuLi_2 , $BF_3 \cdot OEt_2$	CC 1572 (1987)
	R_3Cu_2Li , $BF_3 \cdot OEt_2$	JACS 111 1351 (1989)
	$RCu[P(OMe)_3]_3$	JOC 45 4117 (1980)
	$RCuP(t-Bu)_2Li$	JACS 110 7226 (1988)
	$[Ph_2(Et_2N)Si]CuLi$	JOC 59 4370 (1994)

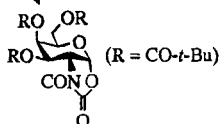
	$(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$ $\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$, TiCl_4 $\text{H}_2\text{C}=\text{CRCH}_2\text{SiMe}_3$, CsF RHgCl , KI , $(\text{K}_2\text{S}_2\text{O}_8)$, $h\nu$	CC 1472 (1987) (2-alken-5-olide) JOC 51 1745 (1986) TL 30 3419 (1989) JOC 54 3768 (1989)
	RLi or $\text{LiCH}_2\text{CO}_2\text{R}'$	JOC 51 1637 (1986)
$\text{CO}_2\text{R}'$, CONR'_2 , CN	$(\text{Me}_4\text{N})\text{PhBR}_3$, $h\nu$ $\text{H}_2\text{C}=\text{CHCH}_2\text{SiMe}_3$, cat $n\text{-Bu}_4\text{NF}$	TL 36 5483 (1995) JOC 51 1745, 1753 (intramolecular) (1986) CC 1472 (1987) (2-alken-5-olide)
$\text{CO}_2\text{R}'$, CN	$(\text{Et}_4\text{N})\text{CCl}_3$ $\text{RCH}_2\text{CH}[\text{B}(\text{OR})_2]\text{ZrClCp}_2$, cat $\text{CuBr}\cdot\text{SMe}_2$ RHgCl , R_3SiH , DMSO $(\text{H}_2\text{C}=\text{CHCH}_2)_2\text{CuLi}$	TL 31 7181 (1990) TL 36 1805 (1995) SL 701 (1993) JOC 51 1745 (1986)
CONHR	RLi ($\text{R} = 1^\circ, 3^\circ$ alkyl; aryl) RMgX ($\text{R} = 1^\circ, 2^\circ, 3^\circ$ alkyl; aryl; allylic; vinylic) RMgBr , cat CuCN $n\text{-Bu}_2\text{Cu}(\text{CN})\text{Li}_2$ $\text{Ph}_2\text{Cu}(\text{CN})_2\text{Li}_2$	JOC 58 7474 (1993) JOC 58 7474 (1993) JOC 51 3921 (1986) JOC 58 7474 (1993) JOC 51 3921 (1986)
CONR'_2	RLi RMgX	JOC 22 1013 (1957) TL 21 1881 (1980) BSCF 1 1087 (1934) JACS 77 4413 (1955) JOC 22 1013 (1957) TL 3251 (1971) TL 36 3227 (1995)
	RCu , Me_3SiI , LiI ($\text{R} = 1^\circ$ alkyl, Ph) R_2CuLi R_2CuLi , Me_3SiCl $(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$	TL 501 (1990); 222 (1991) TL 27 1047 (1986); 32 597 (1991) CC 1472 (1987) (2-alkene-5-lactam)
	$\text{R}_2\text{CuLi}(\text{MgX})$ ($\text{R} = \text{alkyl, aryl}$), Me_3SiCl	JOC 59 6949 (1994)
CSNR'_2	RLi or RMgX	JACS 100 5221 (1978)
CONMeNMe_2	$\text{RCH}(\text{OR})\text{Li}$	TL 31 1981 (1990)
CONHCOCH_3	R_2CuLi , Me_3SiCl	TL 27 1047 (1986)
CONRCOCH_3	RLi , CuI or $\text{CuBr}\cdot\text{SMe}_2$, Me_3SiCl	TL 33 7969 (1992) (2-alkene-4-lactam)
	RMgCl RLi ($\text{R} = \text{alkyl, aryl, vinylic}$), CuI , $n\text{-Bu}_3\text{P}$ / EtAlCl_2 $\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$, TiCl_4	Helv 70 2201 (1987) (chiral) Helv 69 1542 (1986) TL 33 2547 (1992)

XROCH₂

R



RO

CONR₂-*t*-Bu

CN

COCN

RMRMgCl, CuBr·SMe₂ (R = 1°, 2° TL 27 369 (1986)

alkyl; aryl; vinylic)

RCu, Me₃SiLi, LiI (R = 1° TL 36 3227 (1995)

alkyl, Ph)

RCH=CHCu, MgBr₂ TL 31 3645 (1990)Me₃SiCH₂CH=CH₂, TiCl₄ TL 33 2547 (1992)Cp₂ZrCl₂, cat CuBr·SMe₂ Tetr 50 1935 (1994)RCu·BF₃ TL 35 5113 (1994)

RMgX (R = Me, Ar), CuBr, JOC 58 7565 (1993); 60 5509 (1995)

SMe₂

Tetr Asym 4 2315 (1993)

R₂CuMgX (R = Me, Ar) JOC 58 766 (1993)H₂C=CHMgBr, cat CuBr TL 36 3567 (1995)R₂AlCl (R = Et, *n*-Pr, *i*-Bu, SL 343 (1992)

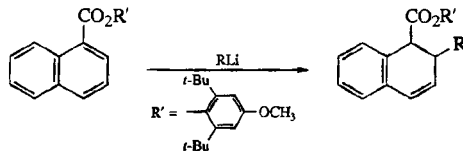
Ph), hv

R₂CuLi SL 64 (1990)(R₃BMe)Li, CuBr TL 255 (1976).Me₂CuLi, Me₃SiCl (product is TL 27 1047 (1986)R'CHMeCH₂COMe)*t*-BuHgCl, NH₄I JACS 117 5967 (1995)H₂C=CRCH₂SiMe₃, TiCl₄/ TL 21 4487 (1980)R'OH (R = H₂C=CRCH₂;X = CO₂R' in product)H₂C=C=CHSiMe₃, TiCl₄/ TL 21 4487 (1980)R'OH (R = HC≡CCH₂;X = CO₂R' in product)RSiMe₃, TiCl₄ (R = allylic, JOC 51 1199 (1986)

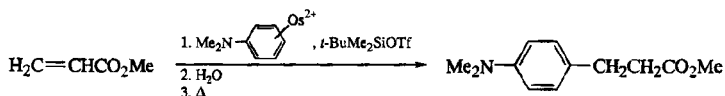
allenic, propargylic, alkynyl;

X = COCN, CO₂H or CO₂Me

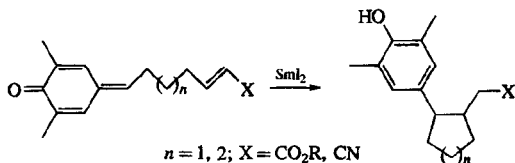
in product)



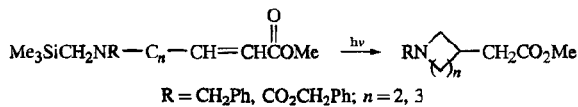
TL 31 1739 (1990); 34 681 (1993)



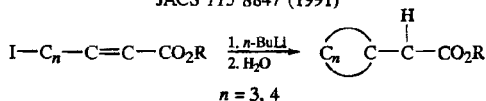
JACS 115 8857 (1993)



JOC 57 6883 (1992)

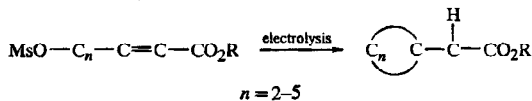


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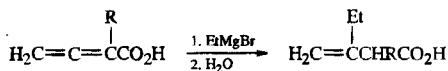


JOC 49 1144 (1984); 57 1495 (1992)

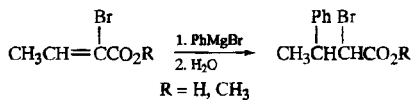
TL 35 2837 (1994)



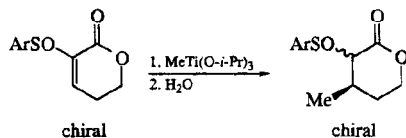
TL 30 2175 (1989)



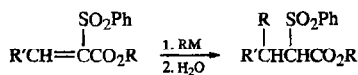
JACS 74 2559 (1952)



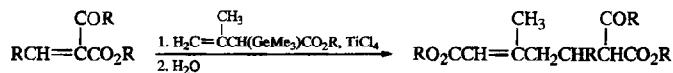
JOC 35 666 (1970)



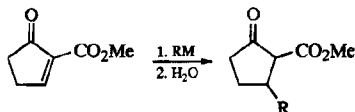
JOC 53 6031 (1988)



TL 33 7407 (1992)



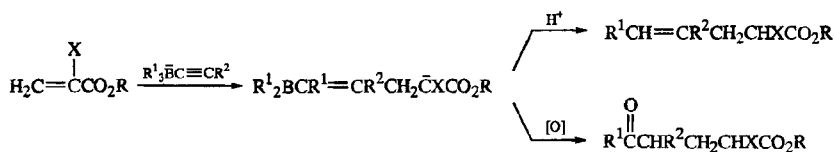
TL 32 4749 (1991)

RM $\text{Et}_2\text{AlC}\equiv\text{CR}$

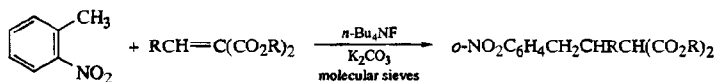
TL 27 2885 (1986)

 Me_2CuLi

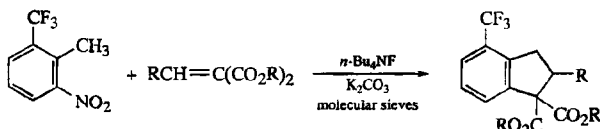
JACS 109 6199 (1987)

X = COMe, CO₂Et

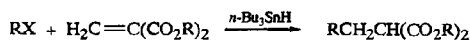
JCS Perkin I 719 (1982)



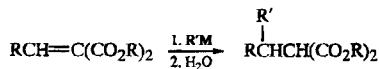
TL 35 6591, 6595 (1994)



TL 35 6595 (1994)



JACS 114 4067 (1992)

R'M

R'Li (R' = 1° alkyl)

CC 464 (1987)

o-NO₂C₆H₄CH₂Na

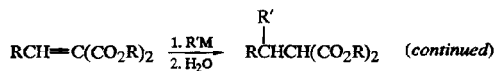
JOC 55 5572 (1990)

MeMgX

CC 464, 1572 (1987)

TL 29 611 (1988)

PhCH_2MgX	JOC 54 3800 (1989)
ArMgX	TL 27 2235 (1986)
$\text{RCH}=\text{CHCH}_2\text{MgX}$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)	JOC 53 3597 (1988)
$\text{RC}\equiv\text{CMgX}$	BSCF 2542 (1964)
$\text{RCH}=\text{CHCH}_2\text{B} \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \text{ (R}' = \text{H}_2\text{C}=\text{CHCHR})$	JOC 53 3597 (1988)
LiAlR_4 ($\text{R}' = 1^\circ$ alkyl)	CC 1572 (1987)
$\text{Li}(\text{Et}_3\text{AlCH}_2\text{CH}=\text{CHOR})$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHOR}$)	JOC 53 3597 (1988)
$\text{H}_2\text{C}=\text{CRCH}_2\text{SiMe}_3$, CsF	TL 30 3419 (1989)
$\text{RCH}=\text{CHCH}_2\text{SnR}_3$, AlCl_3 or SnCl_4 ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)	JOC 53 3597 (1988)
$\text{H}_2\text{C}=\text{CHCH}_2\text{Sn}(n\text{-Bu})_3$, TiCl_4	CC 1572 (1987) JOC 53 3597 (1988)
$\text{RCH}=\text{CHCH}_2\text{Ti}(\text{O-}i\text{-Pr})_3$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)	JOC 53 3597 (1988)
$\text{ROCH}=\text{CHCH}_2\text{Ti}(\text{O-}i\text{-Pr})_3$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHOR}$)	JOC 53 3597 (1988)
$\text{RCH}=\text{CHCH}_2\text{ZrCp}_2\text{Cl}$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)	JOC 53 3597 (1988)
MeMgI , CuCl	Org Syn 50 38 (1970) TL 23 75 (1982) Org Syn Coll Vol 6 442 (1988)
$\text{R}'\text{Cu}$ ($\text{R}' = 1^\circ$ alkyl, vinyl, methallyl)	CC 464 (1987) JAC 114 7652 (1992)
$\text{R}'\text{Cu}$, $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{R}' = 1^\circ$ alkyl, vinyl, methallyl)	CC 464, 1572 (1987) JACS 114 7652 (1992)
$\text{R}'_2\text{CuLi}$ ($\text{R}' = 1^\circ$ alkyl, vinyl, methallyl)	CC 464, 1572 (1987) JACS 114 7652 (1992)
$\text{R}'_2\text{CuLi}$, $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{R}' = 1^\circ$ alkyl, vinyl, methallyl)	CC 464, 1572 (1987) JACS 114 7652 (1992)
$\text{R}'_3\text{CuLi}_2$, $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{R}' = 1^\circ$ alkyl)	CC 1572 (1987)
$\text{R}'\text{Cu}(\text{CN})\text{Li}$ ($\text{R}' = \text{aryl}$, vinyl, methallyl)	TL 27 2235 (1986) JACS 114 7652 (1992)
$\text{R}'\text{Cu}(\text{CN})\text{Li}$, $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{R}' = \text{vinyl}$, methallyl)	JACS 114 7652 (1992)
$\text{R}'_2\text{Cu}(\text{CN})\text{Li}_2$ ($\text{R}' = \text{vinyl}$, methallyl)	JACS 114 7652 (1992)
$\text{R}'_2\text{Cu}(\text{CN})\text{Li}_2$, $\text{BF}_3 \cdot \text{OEt}_2$ ($\text{R}' = \text{vinyl}$, methallyl)	JACS 114 7652 (1992)
$\text{R}'\text{Cu}(\text{CN})\text{ZnX}$	JOC 58 588 (1993) ($\text{R}' = \text{CHRCN}$) TL 36 1023 (1995) ($\text{R}' = \text{CH}_2\text{CH}_2\text{CHROH}$)
$\text{RCH}=\text{CHCu}(\text{CN})\text{ZnI}$	TL 31 4413 (1990)
$\text{ROCH}=\text{CHCH}_2\text{ZnX}$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHOR}$)	JOC 53 3597 (1988)
$\text{RCH}=\text{CHCH}_2\text{ZnBr}$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)	TL 997 (1972)

R'M

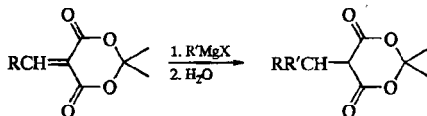
R'ZnX, CuCN·2LiCl (R' = 1° alkyl)

TL 35 1177 (1994)

R'Zn, CuCN·2LiCl (R' = 1° alkyl)

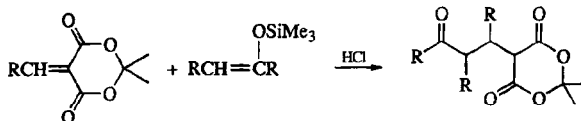
SL 410 (1994)

JOC 60 3311 (1995)

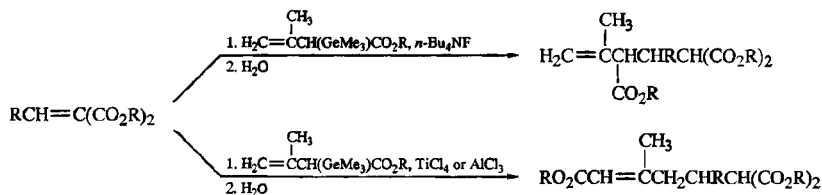


TL 29 611 (1988)

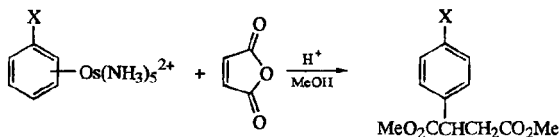
JACS 116 2151 (1994)



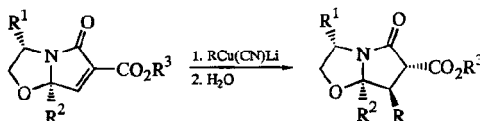
TL 34 7437 (1993)



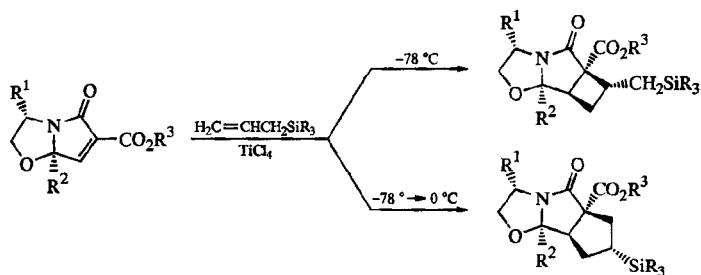
TL 32 4749 (1991)

X = OH, NR₂

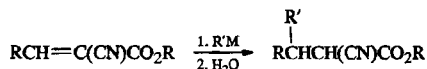
JACS 113 8972 (1991)



JOC 56 3814 (1992); 58 36 (1993)



JOC 59 5144 (1994)

R'M

RMgCl

BSCF II 116 (1982)

TL 35 881 (1994)

 $\text{RCH}=\text{CHCH}_2\text{MgX}$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)

JOC 53 3597 (1988)

 $\text{H}_2\text{C}=\text{CRCH}_2\text{SiMe}_3$, CsF

TL 30 3419 (1989)

 $\text{RCH}=\text{CHCH}_2\text{SnR}_3$, TiCl_4 ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)

JOC 53 3597 (1988)

 $\text{ROCH}=\text{CHCH}_2\text{Ti}(\text{O}-i\text{-Pr})_3$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)

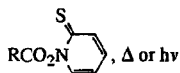
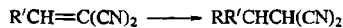
JOC 53 3597 (1988)

 $\text{RCH}=\text{CHCH}_2\text{ZrP}_2\text{Cl}$ ($\text{R}' = \text{H}_2\text{C}=\text{CHCHR}$)

JOC 53 3597 (1988)

 Ar_2CuLi

TL 27 5319 (1986)



SL 441 (1992)

RI, Zn-CuI, ultrasound / H_2O

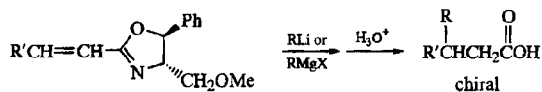
SL 441 (1992)

 $\text{AcOCHRCu}(\text{CN})\text{ZnBr} / \text{H}_2\text{O}$

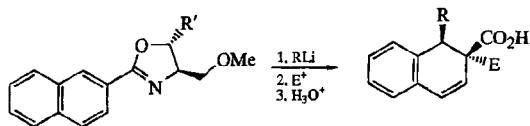
JOC 55 4791 (1990); 58 588 (1993)

 R_3CHgl , KI, *p*-TsOH, $h\nu$

JACS 113 373 (1991); 117 5967 (1995)



JOC 44 2247, 2250 (1979); 46 3874 (1981); 56 7098 (1991)



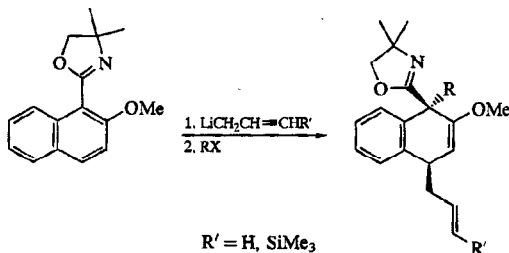
$E^+ = H_2O, RX, RO_2CCl, RSSR$; $R' = Me, Ph$ and other oxazolines

JACS 106 1865 (1984); 110 4611, 7854 (1988)

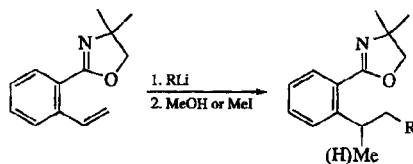
JOC 51 120 (1986); 52 4592 (1987); 59 952 (1994)

Tetr 44 3107 (1988)

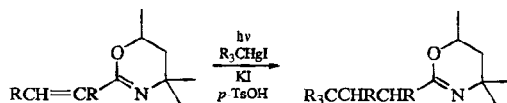
TL 30 4049 (1989); 32 2095 (1991)



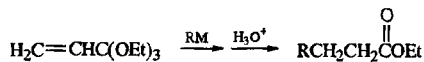
JOC 57 4225 (1992)



JOC 57 5283 (1992)



JACS 113 373 (1991)



RM

$RMgX$, cat $CuBr$

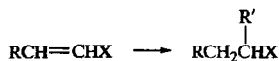
BSCF II 305 (1979)

E - $RCMe=CHAlMe_2$, cat $Pd(PPh_3)_4$, $ZnCl_2$

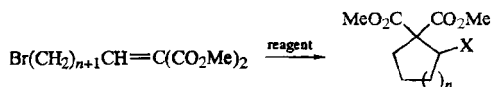
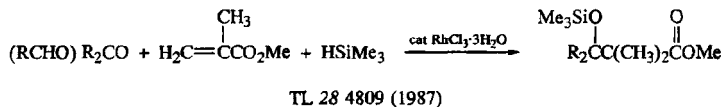
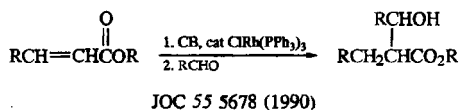
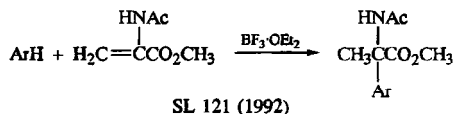
JOC 50 3406 (1985)

$PhZnCl$, cat $Pd(PPh_3)_4$

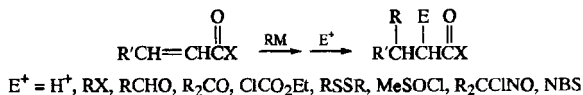
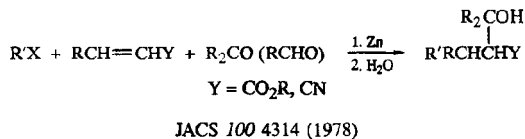
JOC 50 3406 (1985)



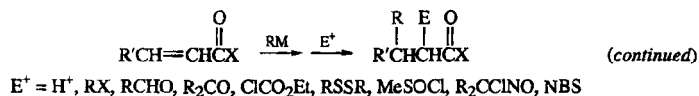
<u>X</u>	<u>Reagents</u>	
CO_2R	$\text{LiHB}(\text{sec-Bu})_3/\text{R}'\text{X}$ $i\text{-Bu}_2\text{AlH}$, cat $\text{MeCu}/\text{MeLi}/\text{R}'\text{X}$	JOC 40 2846 (1975); 41 2194 (1976) JOC 52 439 (1987)
CONR_2	$\text{LiHB}(\text{sec-Bu})_3/\text{R}'\text{X}$	TL 27 4717 (1986)
CN	$\text{LiHB}(\text{sec-Bu})_3/\text{R}'\text{X}$	JOC 55 1479 (1990)

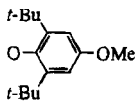
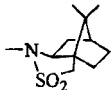



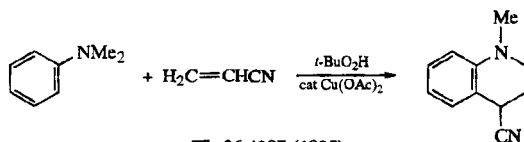
<u>X</u>	<u>Reagent</u>	<u>n</u>	
H	electrolysis	0, 1, 2	TL 23 1339 (1982)
H, CN, $\text{CH}(\text{CO}_2\text{Me})_2$ or $t\text{-BuS}$	$\text{LiHB}(\text{sec-Bu})_3$, KCN, $\text{NaCH}(\text{CO}_2\text{Me})_2$, or $t\text{-BuSLi}(\text{Na})$	1, 2	JOC 47 362 (1982)



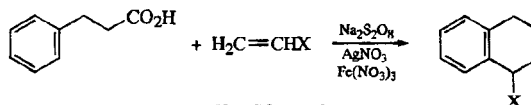
<u>X</u>	<u>RM</u>	
OR'	RMgX , cat CuX ArMgX or Me_2CuLi	CL 1159 (1981) TL 23 3287 (1982)



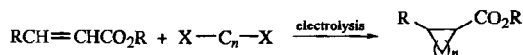
<u>X</u>	<u>RM</u>	
	$\text{RCu}, \text{BF}_3 \cdot \text{OEt}_2$	JACS 109 5820 (1987)
	R_2CuLi	TL 28 3791 (1987)
	$(\text{PhMe}_2\text{Si})_2\text{Cu}(\text{CN})\text{Li}_2$	CC 1472 (1987) (lactone)
	Me_3SnLi	TL 27 5417 (1986)
	$\text{RLi}, \text{LiCH}_2\text{CO}_2\text{R}$	JOC 51 1637 (1986)
	$\text{RCH}=\text{CHRLi}$	JACS 110 5224 (1988)
NHPh	RLi	TL 21 1881 (1980)
NR ₂	RLi, RMgX or $(\text{RS})_2\text{CHLi}$	TL 21 4823 (1980)
	$\text{ArC}(\text{SR})_2\text{Li}$	TL 21 4827 (1980)
	RMgX	CL 913 (1981)
	$\text{R}_2\text{CuLi}, \text{Me}_3\text{SiCl}$	TL 27 1047 (1986)
NMeNMe ₂	RLi	Syn Commun 10 837 (1980)
	RMgCl	Helv 70 2201 (1987)
		TL 31 991 (1990)
	$\text{RMgX}, \text{CuBr} \cdot \text{SMe}_2$	TL 34 2561, 2565 (1993)
		Tetr Asym 4 2315 (1993)
		Syn Commun 25 57 (1995)



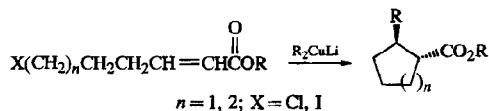
TL 36 4307 (1995)

 $\text{X} = \text{CO}_2\text{R}, \text{CN}$

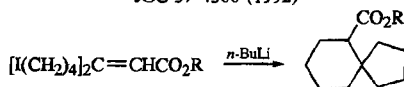
TL 36 4307 (1995)

 $n = 1-4$

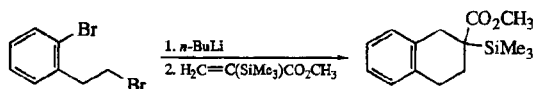
JOC 55 2503 (1990)



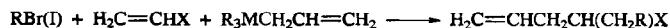
TL 31 4751 (1990)
JOC 57 4300 (1992)



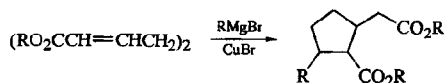
JOC 58 2910 (1993)



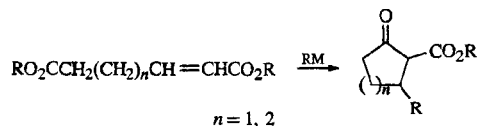
TL 22 3707 (1981)



<u>X</u>	<u>M</u>	<u>Reagents</u>	
$\text{CO}_2\text{R}, \text{CN}$	Pb	—	TL 33 4037 (1992)
	Sn	—	JACS 112 6738 (1990)
	Sn	—	JACS 113 7788 (1991); 114 7664 (1992)
	Sn	$\text{Zn}(\text{OTf})_2, \text{Et}_3\text{B},$ bis(oxazoline)	JACS 117 11029 (1995) (enantioselective)

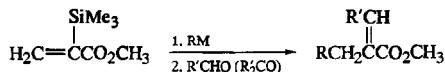


JACS 111 4533 (1989)



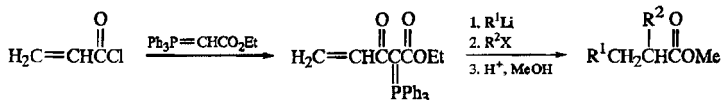
RM

$\text{RMgBr}, \text{CuCl}$	JOC 48 5364 (1983); 57 6981 (1992)
RMgBr, CuI	JACS 111 4533 (1989)
R_2CuLi	JOC 48 5364 (1983); 51 3376 (1986)
$(\text{H}_2\text{C}=\text{CH})_2\text{Cu}(\text{CN})\text{Li}_2$	Org Syn Coll Vol 8 112 (1993)

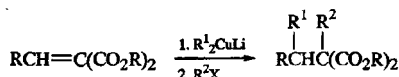


RM = PhMgBr (cat CuCl), $\text{H}_2\text{C}=\text{C}(\text{Li})\text{CH}=\text{CH}_2$, $\text{MeSCH}(\text{Li})\text{SOMe}$

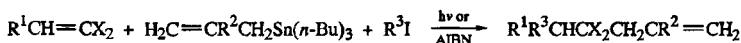
CL 1993 (1984)



JACS 99 642 (1977)

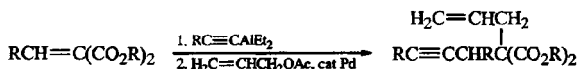


JOC 38 2100 (1973)

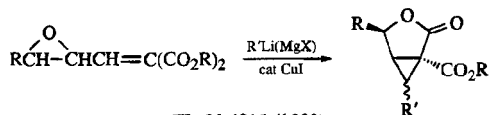


X = CO₂Et, CN

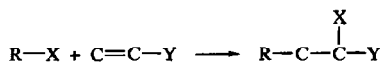
JACS 110 1288 (1988)



TL 34 2271 (1993)

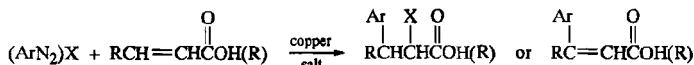


TL 31 4915 (1990)



X = halogen, Y = COR, CO₂R, CN

See page 647, Section 5.

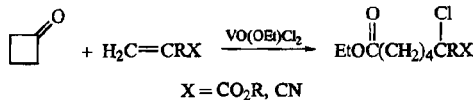


X = halogen

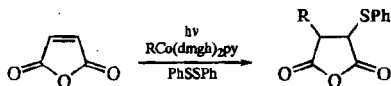
Org Rxs 11 189 (1960); 24 225 (1976) (both reviews)

JOC 52 2997 (1987)

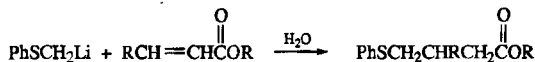
Org Syn Coll Vol 6 21 (1988)



JOC 56 2264 (1991)



TL 35 4071 (1994)



TL 30 3799 (1989)

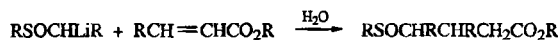
X CO_2R

JOC 57 6301 (1992)

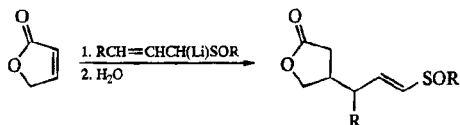
CN

TL 32 2637 (1991)

JOC 57 6301 (1992)



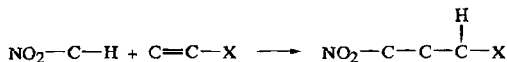
TL 29 5821 (1988); 30 6919 (1989)



JACS 110 5411 (1988)



JOC 58 6716 (1993)

XReagent(s) CO_2R Et_3N , pressure

Angew Int 19 1013 (1980)

DBN

TL 34 7529 (1993)

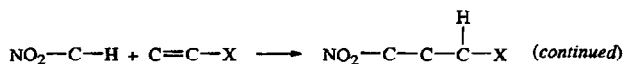
DBU

JOC 50 3692 (1985)

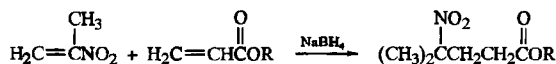
tetramethylguanidine

TL 34 7529 (1993)

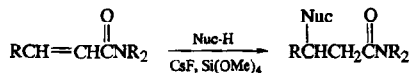
TL 34 7529 (1993)

XReagent(s)

	cat tetramethylguanidine	Syn 44 (1972) JACS 98 6417 (1976) TL 23 2957 (1982) JOC 50 3692 (1985); 54 5128 (1989) Angew Int 20 770 (1981)
	<i>n</i> -Bu ₄ NF·3H ₂ O, pressure	JOC 52 1601 (1987)
	cat KF, alumina	Syn 841 (1982)
	cat NaOH	TL 34 7529 (1993); 35 4413 (1994)
	(PhCH ₂ NMe ₃)OH	Org Syn Coll Vol 4 652 (1963)
	cat (PhCH ₂ NMe ₃)OH	Syn 841 (1982)
	K ₂ CO ₃ , Aliquat [®] 336, ultrasound	SL 907 (1991)
CN	DBU	JOC 50 3692 (1985)
	cat tetramethylguanidine	JOC 50 3692 (1985)
	KOH, (<i>n</i> -Bu ₄ N)HSO ₄	JOC 53 5552 (1988)
SOR	DBU	TL 23 2957 (1982) JOC 47 5017 (1982); 50 3692 (1985)
SO ₂ R	DBU	JOC 50 3692 (1985)
	cat tetramethylguanidine	JOC 50 3692 (1985)

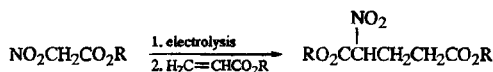


Syn Commun 12 339 (1982)

Nuc-H = RCH₂NO₂, PhCH₂CN, CH₂(CO₂Et)₂, NCCH₂CO₂Et, cyclohexanones

TL 23 5531 (1982)

Tetr 39 999 (1983)



JOC 58 779 (1993)

XReagentNO₂

electrolysis

JOC 58 779 (1993)

COR

KO-*t*-Bu

JOC 57 7175 (1992)

CO₂R

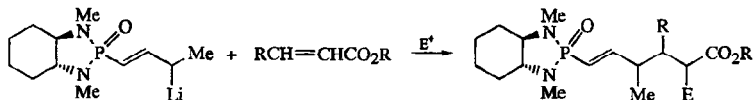
NaOEt

JACS 67 2044 (1945)

CN

KOH

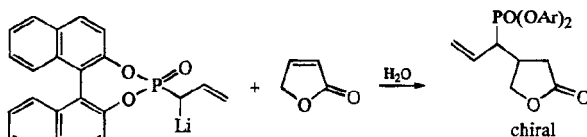
Org Syn Coll Vol 4 776 (1963)

 $E^+ = H^+, RX, RCH=CHCO_2R$

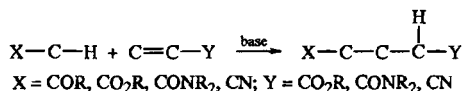
JOC 58 5032 (1993) (esters, lactones, lactams)

TL 35 7509 (1994) (esters)

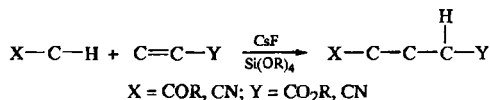
JACS 117 1455 (1995) (lactone)



JOC 60 8036 (1995)

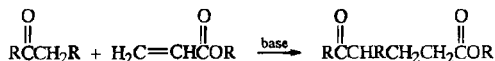


Org Rxns 10 179 (1959) (review)



CC 122 (1981)

Tetr 39 117, 999 (1983)



BSCF 823 (1962)

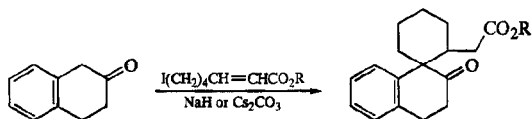
JCS Perkin I 629 (1986)

JACS 110 958 (1988) (intramolecular, chiral)

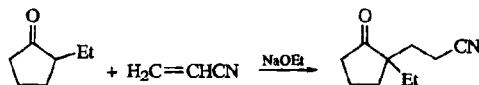
TL 29 5241 (1988); 31 4755 (1990) (intramolecular)

JOC 54 1548 (1989) (intramolecular); 60 4363 (1995)

CL 2171 (1991)



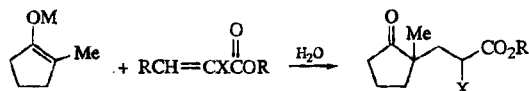
JOC 58 2933 (1993)



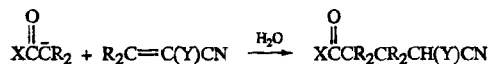
JOC 54 1548 (1989) (intramolecular); 55 798 (1990)

JACS 111 1528 (1989)

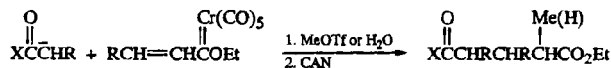
SL 553 (1993)

M = Li, TiCl₃, EtAlCl₂, n-Bu₃Sn; X = SPh, SO₂Ph, CO₂R, CN

TL 34 2421 (1993)

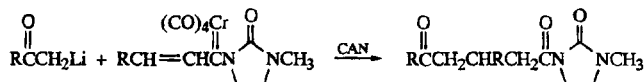
X = R, OR; Y = CO₂R, CN

JOC 51 5480 (1986)

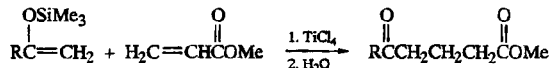


X = R, OEt

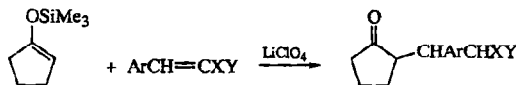
JACS 115 9015 (1993)



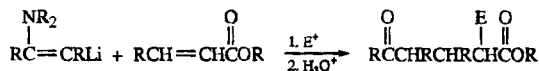
JOC 59 5122 (1994)



BCSJ 49 779 (1976)

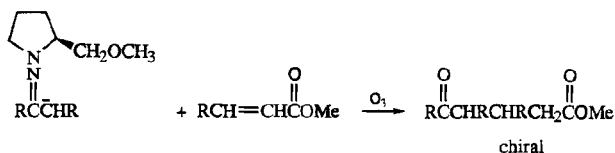
X, Y = H, NO₂, CN, CN

JOC 60 5024 (1995)

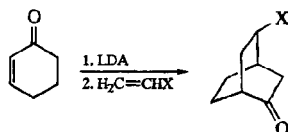
E⁺ = H₂O, RI

Syn 649 (1991)

SL 895 (1992) (chiral amine)



TL 24 4967 (1983); 27 3491 (1986)



X

CO₂R

TL 3333 (1973); 1281 (1986)

BCSJ 48 3769 (1975)

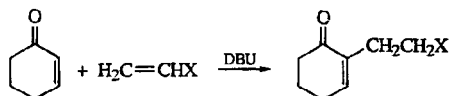
CC 413 (1976); 1212 (1980)

JCS Perkin I 963 (1980); 629 (1986); 373 (1988)

SL 34 (1989); 1017 (1995)

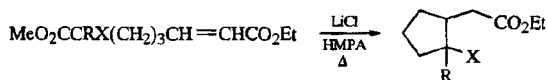
CN, SO₂R

CC 301 (1973)



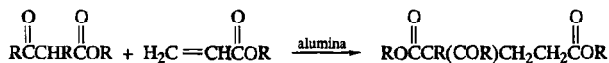
X = CO₂R, CN, SO₂Ph

TL 33 6469 (1992); 35 5397 (1995)

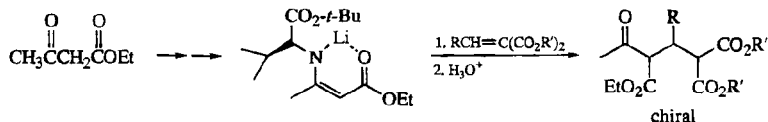


X = COR, CO₂R, CN, SO₂Ph

JOC 58 7143 (1993); 60 2748 (1995)

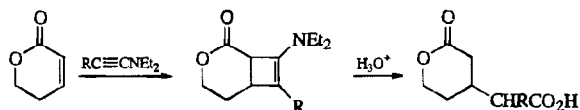


TL 32 2810 (1991)



TL 27 4611 (1986)

CC 1345 (1987)

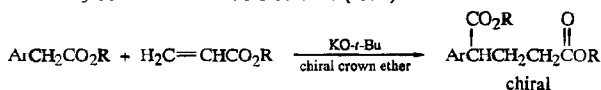


TL 23 1821 (1982)



M = Li, Na, K

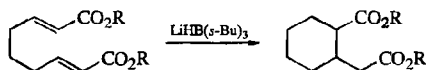
X	E ⁺	
OM	H ⁺	TL 34 1323 (1993)
OR	H ⁺	JACS 62 1763 (1940); 101 1544 (1979); 109 287 (1987) TL 2603 (1973); 4087 (1974); 25 5661 (1984); 26 5025 (1985) (chiral); 27 3551 (1986) (chiral catalysis); 29 2195 (1988) (intramolecular); 30 3857 (1989); 31 3363, 5649 (1990); 32 2165 (1991) (intramolecular); 34 1323 (1993); 35 143 (1994); 36 5951 (1995) (chiral catalysis) J Polym Sci, Polym Chem Ed 17 3509 (1979) Gazz Chim Ital 109 95 (1979) CC 869 (1983) Syn 715 (1983) CL 375 (1984); 2171 (1991) JOC 56 2875 (1991); 58 5301 (1993); 60 3879, 4363, 6700 (1995)
	R'X	TL 26 1723 (1985); 31 3367 (1990) (intramolecular) JOC 60 3879 (1995)
	I ₂	JACS 101 1544 (1979) (2-alken-4-olide)
NR ₂	H ⁺	JACS 96 3702 (1974) TL 27 959 (1986); 31 5649 (1990); 35 143 (1994) CL 2171 (1991) JOC 57 5741 (1992)
	RX	JACS 110 8734 (1988) JOC 55 5433 (1990); 57 2544, 2554, 2566, 2575 (1992)
	Me ₃ SiCl	JOC 60 8140 (1995)



TL 30 7229 (1989)

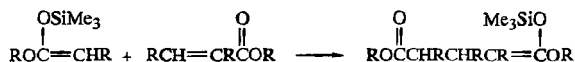


TL 33 2823 (1992)



JOC 57 2888 (1992)

SL 568 (1995)

 $h\nu$

TL 36 7463 (1995)

Al-montmorillonite clay

CC 1203 (1987)

BCSI 61 2157 (1988)

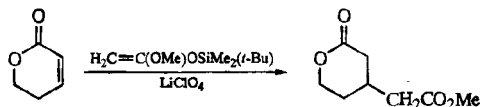
cat $\text{Al}(\text{OTf})_3$

CL 1719 (1987)

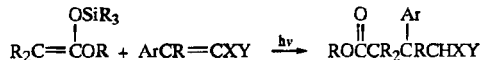
JOC 57 4746 (1992)

cat $n\text{-Bu}_4\text{NF}$

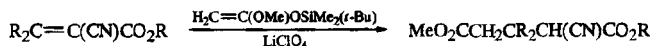
JOC 57 1733 (1992)



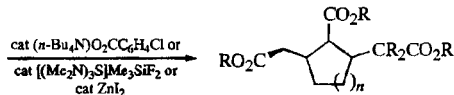
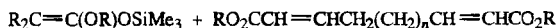
TL 32 4665 (1991)

X, Y = H, CO_2R ; H, CN; CN, CN

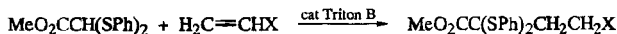
TL 36 7463 (1995)



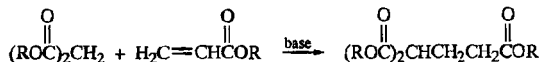
TL 32 4665 (1991)

 $n = 1, 2$

JOC 57 1733 (1992)

X = CN, CO_2R

BSCF II 241 (1982)



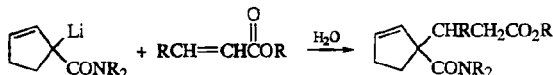
Org Syn Coll Vol 4 630 (1963)

JOC 59 5100 (1994); 60 4363 (1995)

TL 36 7315 (1995) (2-alken-4-olide)



JACS 117 12436 (1995)



CL 1085 (1986)

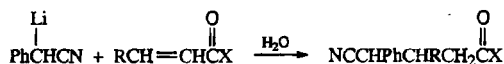
TL 28 1785 (1987)

R = Ph, CO₂R, CN

TL 32 2807 (1991)

X, Y = Ph, CN; CO₂R, CHO; CO₂R, COR; CO₂R, CO₂R; CO₂R, CN; CN, COR

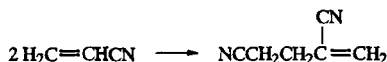
JACS 117 12436 (1995)

X = OR, NR₂

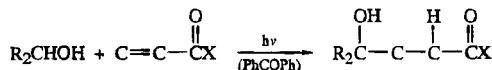
TL 30 4565 (1989)



TL 25 1599 (1984); 29 3095 (1988)



See page 1801, Section 6.

X

OH

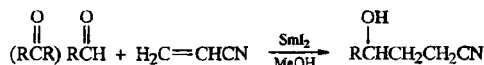
Compt Rend 249 429 (1959)

OR

Angew 69 177 (1957)

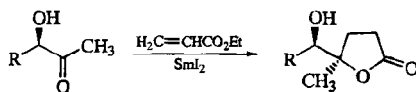
IOC 39 106 (1974) (2-alken-4-olide, 2-alken-5-olide)

SL 67 (1992) (2-alken-4-olide)

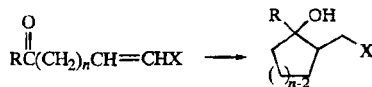


IOC 39 6900 (1994)

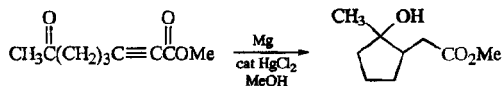
SL 729 (1995)



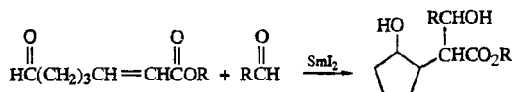
JOC 59 6900 (1994)

X = CO₂R, CN, SPh; n = 3, 4

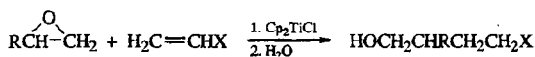
See page 1176, Section 2.2.



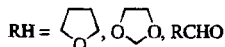
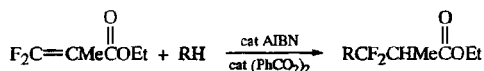
See page 1176, Section 2.2.



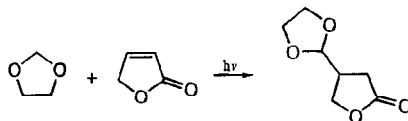
TL 35 1627 (1994)

X = COR, CN, CO₂R

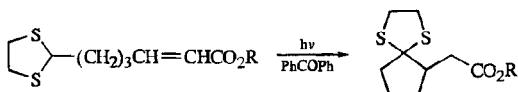
JACS 111 4525 (1989)



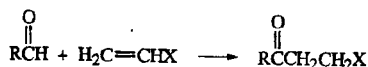
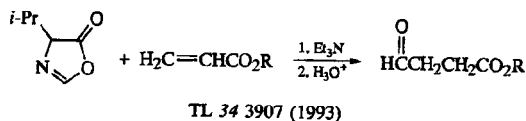
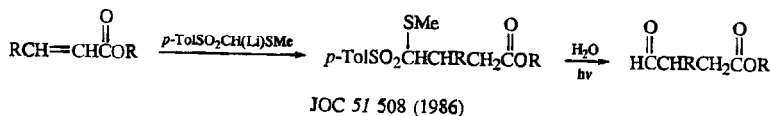
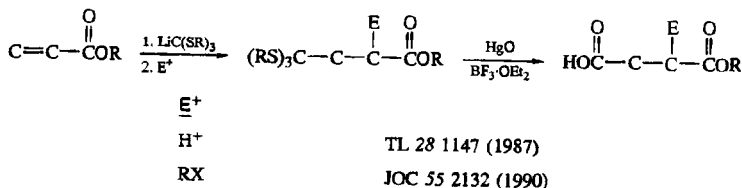
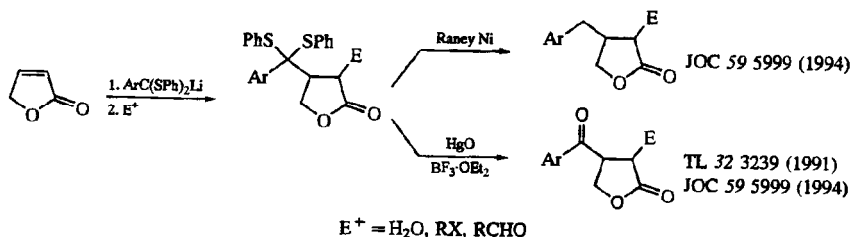
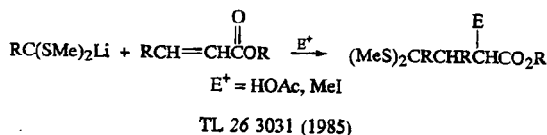
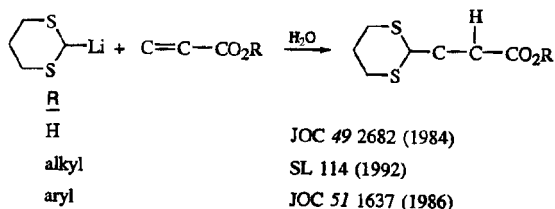
TL 33 1683 (1992)



SL 67 (1992)



TL 31 7035 (1990)

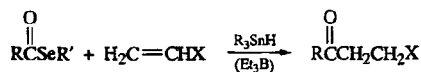


Reviews:

Angew Int 15 639 (1976)
Org Rxns 40 407 (1991)

<u>X</u>	<u>Promoter</u>	
CO ₂ H	hν	Syn 490 (1980)
CO ₂ R	hν	Syn 490 (1980) JOC 52 3323 (1987) TL 31 3063 (1990); 35 7723 (1994) JOC 17 1009 (1952)
	(PhCO ₂) ₂	Org Syn Coll Vol 6 615 (1988)
	cat (PhCO ₂) ₂ , hν	TL 33 1683 (1992)
	cat (PhCO ₂) ₂ , cat AIBN	Angew Int 12 81 (1973)
	cat NaCN	TL 1461 (1973) Ber 109 541 (1976) JOC 57 7044 (1992)
	thiazolium catalyst, base	Ber 109 2890 (1976); 113 2939 (1980) CC 1447 (1986)
	thiazolium catalyst	Angew Int 13 539 (1974) Ber 113 690 (1980); 114 564 (1981) Syn 129, 626 (1981)
CONH ₂	hν	TL 31 3063 (1990)
CN	hν	TL 31 3063 (1990)
	cat NaCN	Angew Int 12 81 (1973) TL 1461 (1973) Ber 107 210 (1974); 109 534 (1976) Org Syn 59 53 (1980) Org Syn Coll Vol 6 866 (1988)
	thiazolium catalyst	Angew Int 13 539 (1974) Ber 109 2890 (1976); 113 690 (1980)

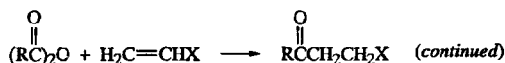
See page 1571, Section 2 for analogous conjugate addition to enones.



<u>X</u>	
CO ₂ R	JOC 53 3377 (1988) (intramolecular); 54 1777 (1989); 57 1492 (1992) JACS 112 9272 (1990) TL 36 31 (1995) (intramolecular)
CN	JOC 54 1777 (1989); 57 1429 (1992)



<u>X</u>	<u>Reagent(s)</u>	
CO ₂ R	electrolysis	JACS 99 7396 (1977)
	cat vitamin B ₁₂ , electrolysis, hν	JACS 105 7200 (1983) Organomet 6 1606 (1987)

XReagent(s)CONH₂cat vitamin B₁₂, electrolysis, hv

Organomet 6 1606 (1987)

CN

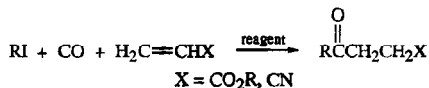
electrolysis

JACS 99 7396 (1977)

cat vitamin B₁₂, electrolysis, hv

JACS 105 7200 (1983)

Organomet 6 1606 (1987)

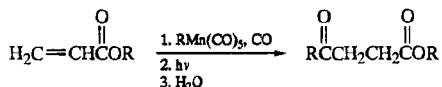
Reagent(Me₃Si)₃SiH

SL 143 (1993); 643 (1994) (intramolecular)

n-Bu₃SnH

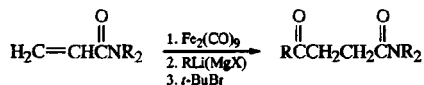
JOC 56 5003 (1991)

SL 643 (1994) (intramolecular)

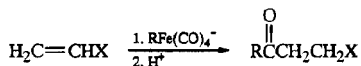


JACS 110 2575 (1988)

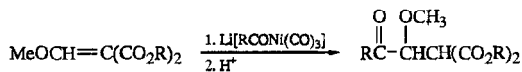
JOC 56 3207 (1991)



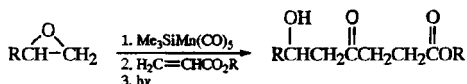
TL 30 2285 (1989)

X = CO₂R, CN

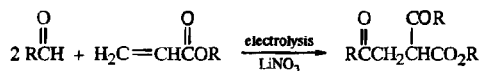
JACS 99 5222 (1977)



JOC 60 1900 (1995)



JOC 53 4892 (1988)



TL 35 4161 (1994)

 E^+

RX

SL 895 (1994)

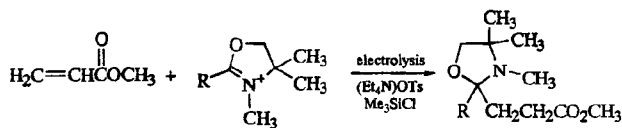
RCHO

SL 651 (1992)

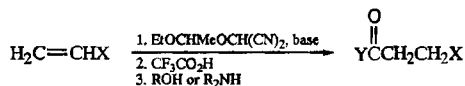
JOC 60 1148, 4585 (1995)

RCOCl

TL 28 3551 (1987)



TL 28 4411 (1987)

 $\text{X} = \text{CO}_2\text{R}, \text{CN}; \text{Y} = \text{OR}, \text{NR}_2$

JOC 56 7195 (1991)

*t*-BuNC, AlCl_3

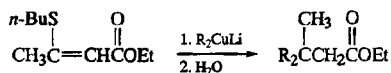
JACS 104 6449 (1982)

 $\text{Me}_2\text{C}(\text{OH})\text{CN}$, KCN, 18-crown-6

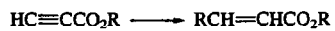
TL 34 7529 (1993)



See page 382, Section 20; page 386, Section 21; and page 392, Section 22.



CC 907 (1973)



See page 410, Section 2.

7. REARRANGEMENTS

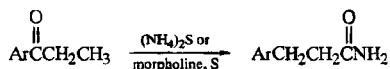
See also page 1861, Section 8 for rearrangements that generate lactones and lactams.

1. Willgerodt and Related Reactions

Review: Angew Int 23 413 (1984)



JOC 60 2456 (1995)

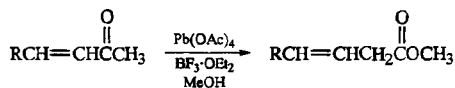


JACS 64 3051 (1942); 68 2029 (1946)

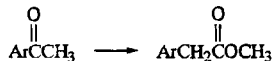
Org Rxs 3 83 (1946)

Angew Int 3 19 (1964)

Newer Methods Prep Org Chem 3 1 (1964)



TL 31 3757 (1990)



I₂, HC(OMe)₃

JOC 53 4858 (1988)

TL 30 3561 (1989)

I₂, HC(OMe)₃, LiClO₄·3H₂O, electrolysis

TL 30 371 (1989)

ICl or ICl₃, HC(OMe)₃

JOC 53 4858 (1988)

Tl(NO₃)₃, CH₃OH

JACS 93 4919 (1971)
JCS Perkin I 235 (1982)
JOC 51 1607 (1986); 53 2620 (1988)
Tetr 48 3735 (1992)

Pb(OAc)₄, BF₃·OEt₂, CH₃OH

Syn 126 (1981)

Pb(OAc)₄, HC(OMe)₃, HClO₄

Syn 456 (1982)
JCS Perkin I 1433 (1987)

AgNO₃, I₂, CH₃OH

JCS Perkin I 235 (1982)



X

Reagents

Cl

hν, H₂O (R' = H)

TL 31 7495 (1990)

Cl, Br

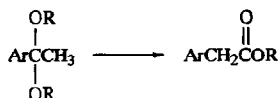
Tl(NO₃)₃·3H₂O, HC(OR')₃

Syn 444 (1983)

Br

Ag⁺, R'OH

TL 23 1385 (1982)

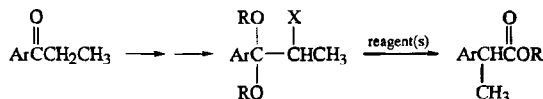


I₂, ICl, or ICl₃; HC(OMe)₃

JOC 53 4858 (1988)

ICl

CC 1311 (1982)



Review: Angew Int 23 413 (1984)

X

Reagent(s)

R

Cl

ZnCl₂

Me

JOC 52 10 (1987)

Cl, Br

ZnX₂ (X = Cl, Br), SnCl₂,
CoCl₂, Hg₂Cl₂, PdCl₂ or
Cu₂Br₂

Me, Et

JOC 48 4658 (1983)

Br

Δ, ROH
AgBF₄, H₂O

Me, -C_n- (n = 2, 3)
H

Syn 505 (1985)
JOC 52 3018 (1987) (chiral)

I

RCO₃H

Me

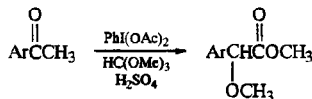
JCS Perkin I 1483 (1983)

RSO₂

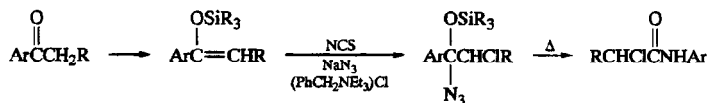
CaCO₃, H₂O, CH₃OH

Me

TL 22 4305 (1981); 23 5427
(1982)



TL 31 3055 (1990)

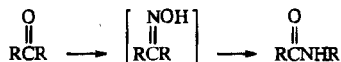


CC 1727 (1987)

2. Baeyer–Villiger

See page 1661, Section 18.

3. Beckmann and Related Reactions



Reviews and key references:

Chem Rev 12 215 (1933); 35 335 (1944)

Org Syn Coll Vol 2 76 (1943)

Org Rxs 11 1 (1960); 35 1 (1988)

P. A. S. Smith, "Molecular Rearrangements," Ed. P. de Mayo, Interscience, New York (1963), Vol 1, p 483

C. G. McCarty, "Chemistry of the Carbon-Nitrogen Double Bond," Ed. S. Patai, Interscience, New York (1970), pp 408–439

R. T. Conley and S. Ghosh, "Mechanisms of Molecular Migrations," Ed. B. S. Thyagarajan, J. Wiley, New York (1971), pp 203–250

Tetr 37 1283 (1981)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 7, Part 5.2, p 689

 $\text{H}_2\text{NOSO}_3\text{H}$

JACS 67 1941 (1945)

JOC USSR 17 2284 (1981)

 $\text{H}_2\text{NOSO}_3\text{H}$, HCO_2H

Syn 537 (1979)

Org Syn 63 188 (1984)

JOC 54 4419 (1989)

Org Syn Coll Vol 7 254 (1990)

 $\text{H}_2\text{NOH}/\text{H}_2\text{SO}_4$

JOC 59 3020 (1994)

 $\text{H}_2\text{NOH}/\text{P}_2\text{O}_5$, MeSO_3H

JOC 38 4071 (1973); 47 3876 (1982)

 $\text{H}_2\text{NOH}/\text{H}_3\text{PO}_4$, Ac_2O

JOC 38 4073 (1973)

 $\text{H}_2\text{NOH}/\text{POCl}_3$

TL 31 2763 (1990)

 $\text{H}_2\text{NOH}/\text{PCl}_5$

JOC 45 3664 (1980); 59 1418 (1994)

 $\text{H}_2\text{NOH}/\text{TsCl}$, NaOH

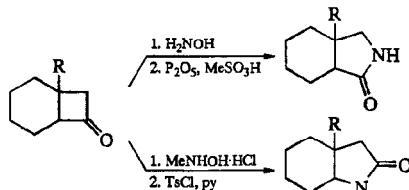
JOC 60 279 (1995)

 $\text{H}_2\text{NOH}/\text{TsCl}$, py, cat DMAP

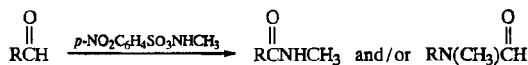
JACS 106 6414 (1984)

JOC 57 4110 (1992)

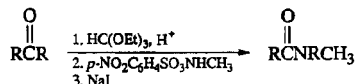
$\text{H}_2\text{NOH}/\text{TsCl}, \text{py}/\text{Et}_3\text{N}$	JACS 106 6702 (1984)
$\text{H}_2\text{NOH}/\text{TsCl}/\text{SiO}_2$	JACS 112 323 (1990)
$\text{H}_2\text{NOH}/\text{MsCl}, \text{Et}_3\text{N}$	TL 30 7233 (1989)
$\text{H}_2\text{NOH}/\text{AlI}_3$	TL 31 1063 (1990)
$\text{H}_2\text{NOH}/\text{K-10 montmorillonite}, \text{microwave irradiation}$	SL 1259 (1995)



JOC 47 3876, 3881 (1982)



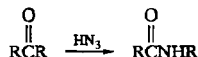
JOC 57 4487 (1992)



TL 32 2429 (1991)

4. Schmidt

For the synthesis of lactams, see page 1861, Section 8.



Reviews:

Org Rxs 3 307 (1946)

P. A. S. Smith, "Molecular Rearrangements," Ed. P. de Mayo, Interscience, New York (1963), Vol 1, pp 507-527

D. V. Banthorpe, "Chemistry of the Azido Group," Ed. S. Patai, Interscience, New York (1971), p 397

Russ Chem Rev 40 835 (1971)

Tetr 37 1283 (1981)

JACS 67 1941 (1945)

TL 29 403 (1988) (3-oxoalkanoate ester to 2-(acylamino)alkanoate ester); 32 2469 (1991)

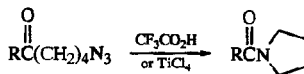


BF_3

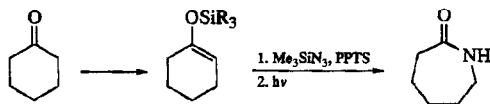
JACS 117 8047 (1995)

TiCl_4

JOC 57 1635 (1992) (cyclic ketones)



JACS 113 8965 (1991); 117 10449 (1995)
JOC 58 2933 (1993)

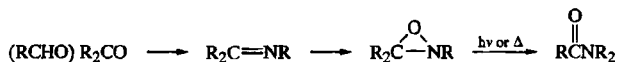


JOC 60 6662 (1995)

5. Curtius

See page 868, Section 1.2.

6. Oxaziridine \longrightarrow Amide



JACS 79 5739 (1957); 104 3929 (1982); 112 4879 (1990); 116 6439, 9009 (1994); 117 5169, 7812 (1995)
Compt Rend C 273 1097 (1971); 275 581 (1972)

Syn 812 (1974)

TL 851 (1975); 28 2595 (1987); 29 151, 4511 (1988) (both chiral lactams); 31 2965 (1990); 34 6773 (1993)

J Heterocyclic Chem 13 623 (1976); 17 1025 (1980)

Nouv J Chim 3 739 (1979)

Adv Heterocyclic Chem 24 63 (1979) (review)

Tetr 45 5703 (1989) (review)

JOC 56 499 (1991)

7. Favorski and Related Reactions

Review: "Comprehensive Organic Chemistry," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 3.7, p 839



Org Rxs 11 261 (1960) (review)

BSCF 755, 763, 773 (1963)

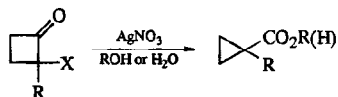
Org Syn Coll Vol 4 594 (1963)

Acta Chem Scand 21 163 (1967)

Russ Chem Rev 732 (1970) (review)

JOC 47 4485 (1982); 52 4885 (1987); 53 4021 (1988)

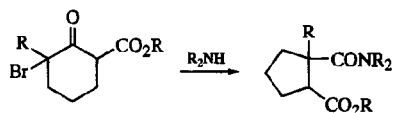
JACS 109 7230 (1987)



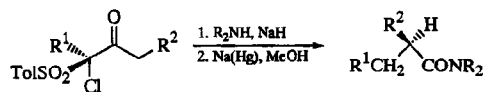
$\text{X} = \text{Cl, Br}$

Acta Chem Scand 21 163 (1967)

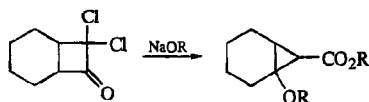
JOC 42 4157 (1977); 53 4877 (1988)



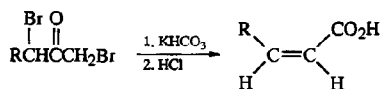
JOC 54 5544 (1989)



TL 34 4823 (1993)

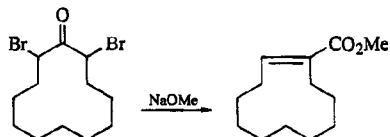


TL 1071 (1970); 34 8157 (1993)

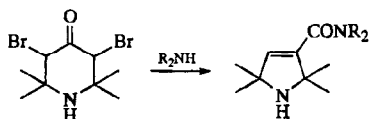


Acta Chem Scand 19 383 (1965)

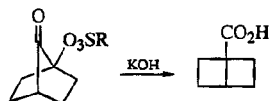
Org Syn Coll Vol 6 711 (1988)



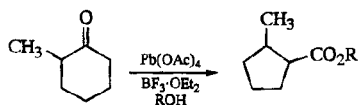
Org Syn Coll Vol 6 368 (1988)



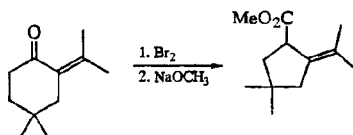
JOC 54 3667 (1989)



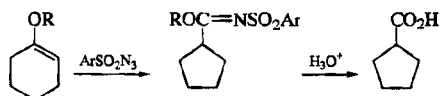
Tetr 42 1621 (1986)



Syn 898 (1979)



JOC 46 5434 (1981)

R

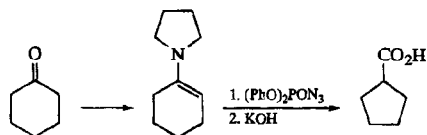
Me

TL 3111 (1973)

 Me_3Si

Helv 56 1826 (1973)

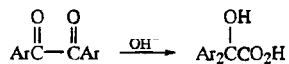
JOC 47 5042 (1982)



TL 4749 (1976)

Org Syn Coll Vol 7 135 (1990)

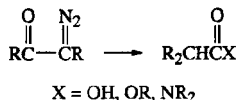
8. Benzilic Acid



Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 3.6, p 821

9. Arndt-Eistert and Wolff

Review: "Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 3, Part 3.9, p 887



Reviews and key references:

Newer Methods Prep Org Chem 1 513 (1948); 3 451 (1964)

Angew 72 535 (1960)

Fortschr Chem Forsch 5 1 (1965)

Russ Chem Rev 36 260 (1967)

Adv Alicyclic Chem 3 125 (1971) (ring contraction)

"Carbenes," Eds. M. Jones Jr. and R. A. Moss, J. Wiley, New York (1973), Vol 1, p 117

Angew Int 14 32 (1975)

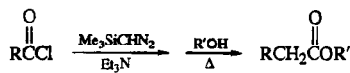
JACS 101 7675 (1979) (ring contraction)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, New York (1991), Vol 3, Part 3.9, p 887

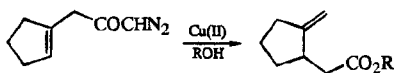


Review: Org Rxns 1 38 (1942)

<u>X</u>	<u>Reagents</u>	
OH	hν, H ₂ O	Org Rxns 1 38 (1942) (review) Ber 91 430 (1958) Org Syn Coll Vol 6 840 (1988) JACS 112 8889 (1990) JACS 113 3513 (1991) JOC 57 1067 (1992); 58 471 (1993) Org Rxns 1 38 (1942) (review) TL 2667 (1979)
	AgOAc, H ₂ O	
	AgNO ₃ , H ₂ O	
	Ag ₂ O, H ₂ O	
	Ag ₂ O, Na ₂ CO ₃ , Na ₂ S ₂ O ₃ , H ₂ O	
OR	hν, ROH	JACS 107 5732 (1985); 109 4626 (1987); 110 6785, 7217 (1988); 112 9645 (1990); 117 9804 (1995) JOC 57 252 (1992); 60 6953 (1995) Org Syn 50 77 (1970) TL 2667 (1979) JACS 109 5432 (1987) Org Syn Coll Vol 6 613 (1988) JOC 54 1548 (1989); 57 3463 (1992)
	AgO ₂ CPh, Et ₃ N, ROH (R = Me, Et)	
NH ₂	hν/NH ₄ OH	JACS 106 6437 (1984)
	AgNO ₃ , NH ₄ OH	JOC 5 606 (1940)
NR ₂	hν, R ₂ NH	TL 29 6113 (1988) JOC 60 3249 (1995)



TL 21 4461 (1980)



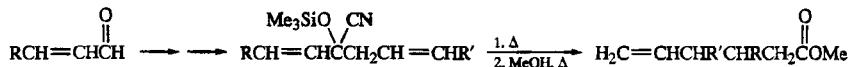
JACS 106 3995, 4001 (1984)



TL 30 2153 (1989); 32 1495 (1991); 34 3589 (1993)

JOC 58 7170 (1993)

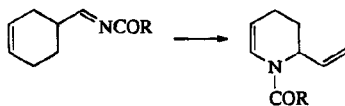
10. Cope



TL 21 2125 (1980); 22 1179 (1981)

JACS 106 718 (1984)

11. Aza-Cope



JOC 53 963 (1988)

12. Claisen

Reviews:

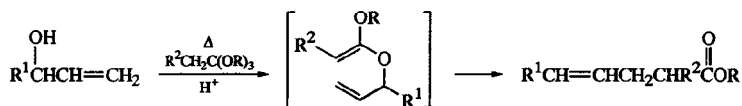
Syn 589 (1977)

Acct Chem Res 10 227 (1977)

R. K. Hill, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Part B, Chpt 8 (chirality transfer)

Chem Rev 88 1423 (1988)

"Comprehensive Organic Synthesis," Eds. B. M. Trost and I. Fleming, Pergamon, Oxford (1991), Vol 5, Part 7.2, p 827



JACS 92 741 (1970); 98 1583 (1976); 100 8272 (1978); 101 3066 (1979); 102 6891 (1980); 103 2419, 5259 (1981); 108 1039, 4603 (1986); 109 3025 (1987); 110 5434 (1988); 111 2596, 7504, 8231, 8263 (1989); 116 9019 (1994); 117 3448 (1995)

CC 1512, 1513 (1970); 858 (1979); 123 (1982)

TL 1281 (1973); 691 (1975); 2543 (1977); 2575 (1978) (allenic alcohol); 3057 (1979); 21 1285, 4335 (1980); 23 947, 3531 (1982); 28 2597 (1987); 32 5525 (1991); 35 4951 (1994); 36 757, 8723 (1995)

JOC 39 3315 (1974); 41 3497 (1976); 43 3435 (1978); 44 3374 (1979); 45 891, 2080 (1980); 46 1485, 3896 (1981); 47 337, 620, 2420 (1982); 48 1829 (1983); 51 3402, 5429 (1986); 52 1201, 3541 (1987); 53 1922 (1988); 54 1223, 3354 (1989); 55 2108, 3968 (1990); 58 1003 (1993)

BSCF 2040 (1974) (allenic alcohols)

CL 1721 (1981); 1113 (1982)

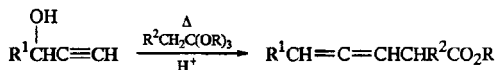
JCS Perkin I 2909 (1982)

Syn Commun 12 395 (1982)

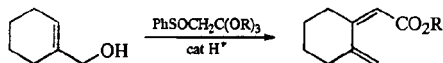
Org Syn 64 175 (1985)

Org Syn Coll Vol 6 584, 606 (1988); 7 164 (1990)

SL 453 (1990); 279 (1991); 217, 489 (1992)

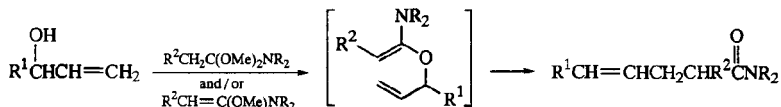


JOC 53 4736 (1988)



JOC 56 6981 (1991); 59 7855 (1994)

Bio Med Chem Lett 3 1829 (1993)



Helv 47 2425 (1964); 52 1030 (1969); 62 1922 (1979)

Ber 104 3679 (1971)

BSCF 2040 (1974) (allenic alcohols)

JOC 42 3828 (1977); 49 2682 (1984); 52 1372 (1987); 53 1922, 4282 (1988); 55 863 (1990); 57 7133 (1992); 58 3840 (1993)

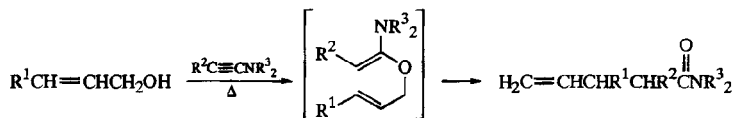
TL 23 109 (1982); 27 3053 (1986); 28 789 (allenic alcohol), 2041 (1987); 31 869, 5829 (1990); 32 5525 (1991)

Angew Int 24 700 (1985) (allenic alcohol)

CC 1759 (1986)

Org Syn Coll Vol 6 491 (1988)

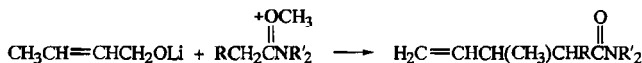
JACS 111 2596 (1989); 117 11106 (1995)



TL 5425 (1966)

Compt Rend C 268 1446 (1969) (allenic alcohol)

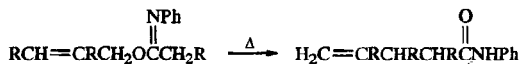
IOC 44 882 (1979); 46 3896 (1981)



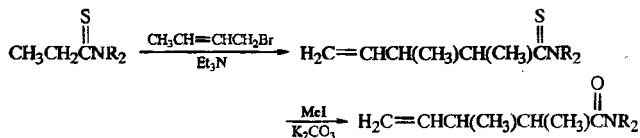
JOC 50 5909 (1985)

JACS 109 6716 (1987)

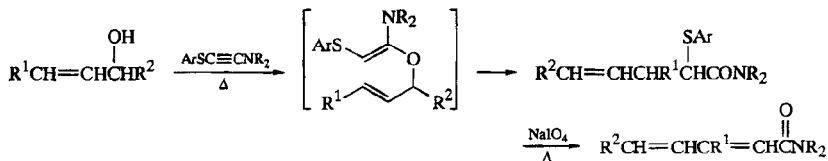
TL 32 4267 (1991)



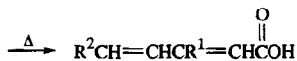
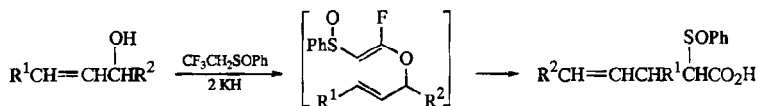
See page 1857, Section 15.



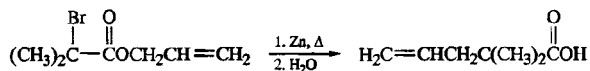
JACS 109 6716 (1987)



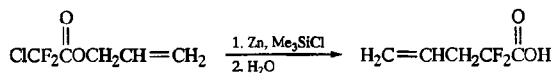
TL 22 4097 (1981)



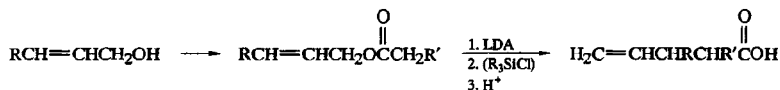
CL 1289 (1981)



CC 117 (1973)



TL 29 3291 (1988)



JACS 71 1150, 2439 (1949); 94 5897 (1972); 98 2868 (1976); 102 1155 (R' = OR), 6889, 6891 (1980); 103 3205 (1981); 104 1124, 4030 (1982); 106 3668, 5002 (1984); 107 1448, 3271, 3279, 3285 (1985); 108 2105, 2662 (1986); 111 2599, 3712 (1989); 112 5583 (1990); 113 6594 (1991) (R' = Me, MeO); 115 7152, 7166 (1993); 116 9019 (1994)

Syn Commun 2 27 (1972)

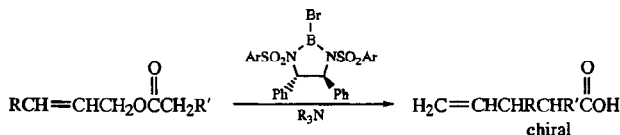
JOC 39 3315 (1974); 41 986 (1976); 43 784 (1978) (R' = OR); 45 48, 4259 (1980); 46 479, 3896 (1981); 47 337, 3933 (R' = RCONH), 3941 (R' = OH, OR) (1982); 48 1829, 5221 (R' = OR) (1983); 50 1128 (1985) (R' = OR); 51 503, 1152 (R' = OR), 3247, 4023, 4322, 4485, 5019 (1986); 52 3889 (1987) (R' = OR); 53 1922, 4085, 4282 (1988); 54 1789 (1989); 56 353 (α -fluoro esters), 650, 3431, 3572, 5755, 5826 (1991); 57 2228, 4323, 5778, 5947, 6696 (1992); 58 1003, 4589, 5301, 5873, 6255 (1993); 59 332, 1160, 3270 (1994); 60 3288, 5093 (1995)

TL 3975 (1975); 2839 (1977); 23 619 (R' = RCONH), 623 (R' = RCONH), 2825, 3419 (R' = OH, PhS), 3799, 4309, 5455 (1982); 24 729 (R' = OH), 5177 (R' = OR) (1983); 25 1543, 5155 (R' = OH) (1984); 27 3345 (1986); 28 1035, 1439, 1925, 3031, 4143 (R' = OR), 4147 (R' = OR), 4629 (1987); 29 1375, 2539, 5151 (1988); 30 515, 4193 (1989); 31 869 (1990); 32 2909, 3209, 5953, 7601 (1991); 33 6259 (1992); 34 2251, 3985, 6545, 8209 (1993); 36 5035 (1995)

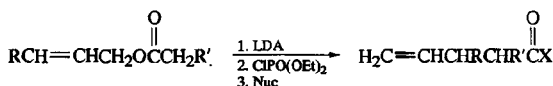
CL 1721 (1981)

BCSJ 55 3555 (1982)

CC 1220 (1987)

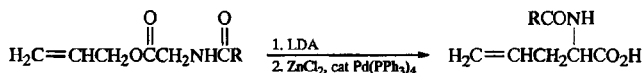
SL 81 (B, Sn enolates; R' = OR), 479 (1992); 1138 (1995) (R' = NHCO₂R, Al enolate)

JACS 113 4026 (1991); 117 193 (1995)



Nuc = ROH, RSH, HN(Me)OMe; X = OR, SR, N(Me)OMe

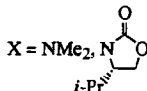
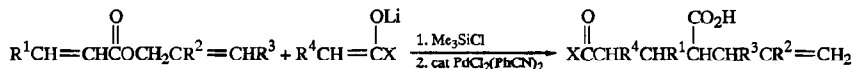
JACS 115 8847 (1993)



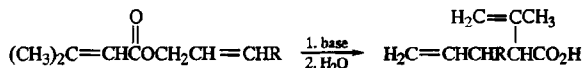
JOC 59 6667 (1994)



RM

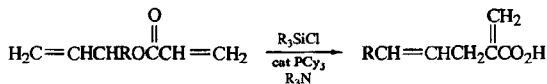
RMgX, cat Cu(*o*-OC₆H₄CH=N-*i*-Pr)₂, Me₃SiCl TL 31 7457 (1990)RCu (LiI), Me₃SiI SL 271 (1994)R₂CuLi (LiI), Me₃SiCl SL 271 (1994)

JOC 60 8140 (1995)

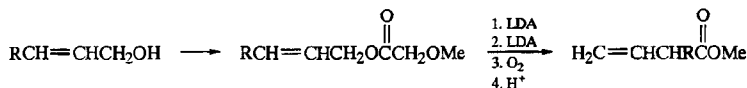


JOC 40 3309 (1975); 57 4380 (1992)

Chimia 29 528 (1975)



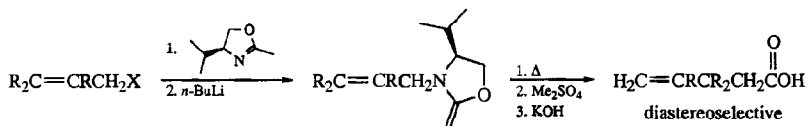
JOC 58 299 (1993)



CC 594 (1977)

JOC 43 784 (1978); 45 4135 (1980)

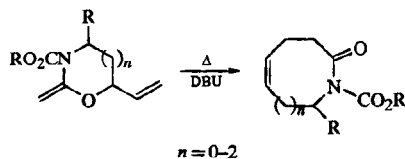
13. Aza-Claisen and Related Rearrangements



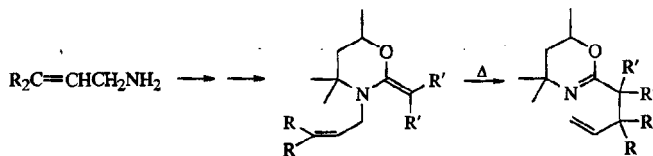
JACS 107 443 (1985)

JOC 50 5769 (1985); 51 1377 (1986)

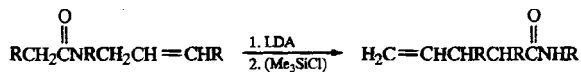
TL 28 1031 (1987)



TL 33 6857 (1992)

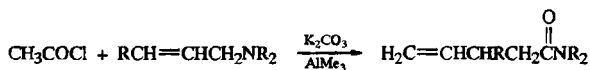


IOC 39 421 (1974)

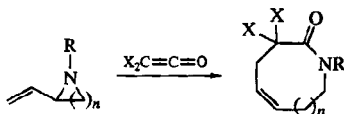


TL 31 727 (1990); 33 1651 (1992); 34 3297 (1993)

Pure Appl Chem 62 1405 (1990)



IOC 60 3773 (1995)



See page 1861, Section 8.

Ph₃P, CX₄ (X = Cl, Br), Et₃N

TL 34 1453 (1993)

Ph₃P·Br₂, Et₃N

TL 34 1453 (1993)

Ph₃P, I₂, Et₃N

TL 34 1453 (1993)

P(OEt)₃, I₂, Et₃N

TL 34 1453 (1993)

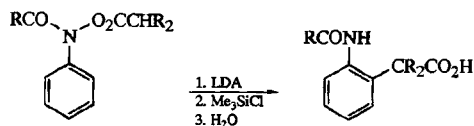
JOC 59 2645 (1994)

Ti₂O, *i*-Pr₂NEt

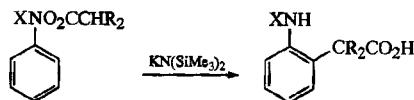
TL 34 1453 (1993)

triposgene, Et₃N

TL 34 1453 (1993)



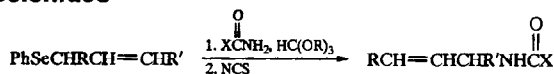
TL 32 2671 (1991)



X = R, COR

TL 32 2803 (1991)

14. Allylic Selenides

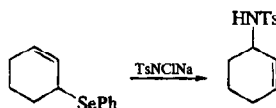
X

OR

CH(OMe)Ph

JOC 51 5243 (1986); 52 3759 (1987)

JOC 51 5243 (1986)



JOC 51 5243 (1986)

15. Imidate Esters



Review: Acct Chem Res 13 218 (1980)

X Reagent

F A

CC 717 (1989)
TL 34 6769 (1993)

Cl A

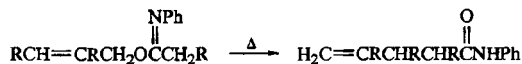
JACS 96 597 (1974); 98 2901 (1976); III 4829 (1989)
BCSJ 49 3247 (1976)
Org Syn 58 4 (1978)
CC 770 (1984)
JOC 52 1487, 5127 (1987); 57 1682 (1992); 58 795 (1993)
Org Syn Coll Vol 6 507 (1988)
TL 35 3049 (1994); 36 2975, 3461, 4311 (1995)

XReagent

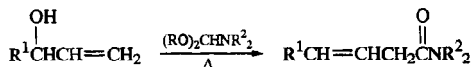
cat $\text{Hg}(\text{O}_2\text{CCF}_3)_2$ JACS 96 597 (1974); 98 2901 (1976)
 cat $\text{PdCl}_2(\text{PhCN})_2$ Angew Int 23 579 (1984)
 TL 33 4313 (1992)
 cat $\text{Pd}(\text{O}_2\text{CR})_2$ ($\text{R} = \text{CH}_3, \text{CF}_3$) JOC 58 795 (1993)

Reagent

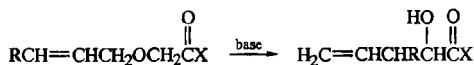
Δ Ber 70 2214 (1937)
 TL 36 2975 (1995)
 cat $\text{Pd}(\text{PPh}_3)_4$ CL 1815 (1982)
 cat $\text{PdCl}_2(\text{PhCN})_2$ CL 1815 (1982)
 TL 36 2975 (1995)



Δ Tetr 44 6841 (1988)
 $\text{LiNEt}_2 / t\text{-BuMe}_2\text{SiCl} / \text{H}_3\text{O}^+$ SL 97 (1990)

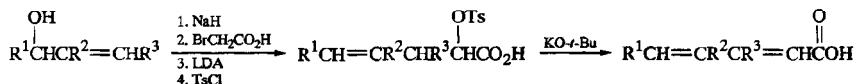
16. 2,3-Sigmatropic Rearrangement

JACS 96 5563 (1974)
 JOC 42 3828 (1977)

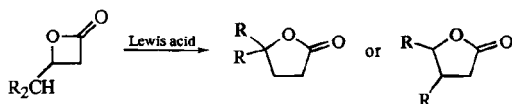


$\text{X} = \text{OH}, \text{OR}, \text{NR}_2$

See page 1063, Section 5.



TL 22 69 (1981)



Lewis acid

$MgBr_2$

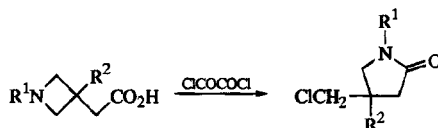
TL 28 4787 (1987); 29 1747 (1988); 31 6617 (1990);
36 3679 (1995)

JOC 53 2371, 5922 (1988)

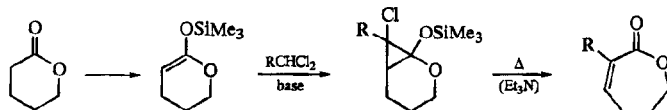
$TiCl_4$

TL 31 6617 (1990)

See also page 1861, Section 8.



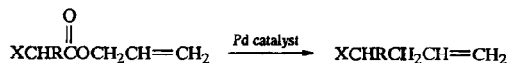
TL 32 4799 (1991)



$R = H, F, CH_3$

JOC 55 4807 (1990)

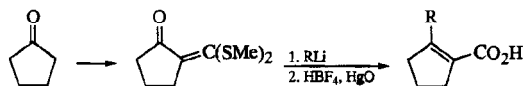
20. Decarboxylation-Allylation



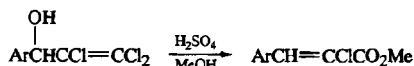
$X = CN, CO_2R$

JOC 52 2988 (1987)

21. Other Reactions



TL 23 3747 (1982)



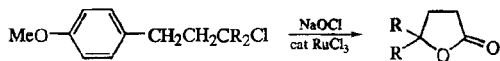
JOC 56 3323 (1991)

8. LACTONE AND LACTAM FORMATION

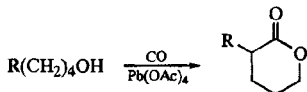
Reviews:

- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol XI/2 (lactams), G. Thieme, Stuttgart (1958)
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol VI/2 (lactones), G. Thieme, Stuttgart (1963)
- Syn 67 (1975) (α -methylene lactones); 441 (1993) (β -lactones)
- Tetr 33 683, 3041 (1977) (both macrocyclic lactones); 34 1731 (1978) (β -lactams); 44 5615 (1988) (β -lactams); 51 2777 (1995) (medium ring lactones)
- Angew Int 16 585 (1977) (macrolides)
- Org Prep Proc Int 13 59 (1981) (saturated γ -lactones); 27 307 (1995) (β -lactones)
- H. M. Colquhoun, D. J. Thompson, M. V. Twigg, "Carbonylation-Direct Synthesis of Carbonyl Compounds," Plenum, New York (1991), Chpts 9 and 10
- Houben-Weyl, "Methoden der Organischen Chemie," 4th ed, Vol E16b (β -lactams), G. Thieme, Stuttgart-New York (1991)
- "The Chemistry of β -Lactams," Ed. M. I. Page, Blackie Academic and Professional/Chapman and Hall, London (1992)
- M. A. Ogliaruso, J. F. Wolfe, "Synthesis of Lactones and Lactams. Updates to the Chemistry of Functional Groups," J. Wiley & Sons, New York (1993)
- Contemporary Organic Synthesis 1 417 (1994) (β -lactams)

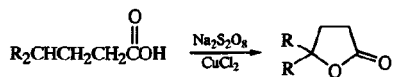
See also page 1650, Section 14, for diols to lactones and page 1652, Section 15 for amino alcohols to lactams.



TL 29 6925 (1988)



JACS 116 5473 (1994)



JCS Perkin II 595 (1983)

Br₂, AIBN

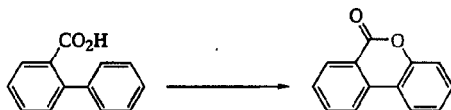
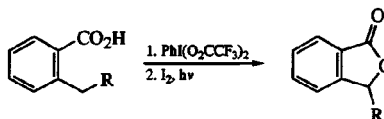
TL 29 85 (1988)

K₂S₂O₈

SL 421 (1990)

DDQ

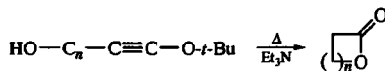
TL 28 5175 (1987)



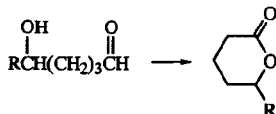
TL 36 7089 (1995)

 $n = 1, 2$

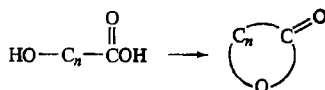
TL 31 201 (1990)

SL 36 (1989) ($n = 13$)TL 34 2071 (1993) ($n = 10$) $n = 3\text{--}8, 10, 12$

SL 743 (1994)



See page 1670, Section 19.

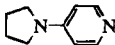



Reviews:

Houben-Weyl, Vol VI/2 (1963), p 511

Tetr 33 683, 3041 (1977)

Angew Int 18 707 (1979)

- lipase TL 29 5583 (1988)
- HCl JACS 94 5815 (1972)
- cat TsOH Helv 17 1283 (1934); 18 1087 (1935)
- TsOH, microemulsion JOC 46 2594 (1981)
- PhSO₂Cl, py JACS 94 2000 (1972)
CC 52 (1979); 1199 (1986)
JOC 53 2371 (1988); 56 5778 (1991)
TL 31 3645 (1990); 36 3679 (1995)
- p*-BrC₆H₄SO₂Cl, py JOC 54 2311 (1989); 56 1280 (1991); 59 3642 (1994)
- MeSO₂Cl, Na₂CO₃ JCS Perkin I 884 (1976)
- Tf₂O, py SL 119 (1993)
JOC 59 3762 (1994)
- n*-Bu₂SnO JACS 102 7578 (1980); 105 7130 (1983)
- n*-Bu₂SnO-*n*-Bu₂SnCl₂ TL 27 4501 (1986)
- (CF₃CO)₂O Tetr 24 2443 (1968)
- (CH₃)₃CCOCl, Et₃N/  JOC 48 758 (1983)
- 2,6-Cl₂C₆H₃COCl, Et₃N/DMAp TL 28 2409 (1987)
JOC 58 7170 (1993)
- 2,4,6-Cl₃C₆H₂COCl, R₃N/DMAp CL 1021 (1979)
BCSJ 52 1989 (1979)
TL 22 2679 (1981); 25 2163 (1984); 28 4569 (1987);
29 1461, 5139 (1988); 32 517, 1499 (1991); 35
6503 (1994); 36 147, 3361 (1995)
Tetr 46 4613 (1990)
JOC 55 7 (1990); 56 5132 (1991); 58 4555, 7789
(1993); 59 949 (1994)
SL 614, 618 (1991); 503, 840 (1992); 407 (1995)
JACS 113 5478 (1991); 114 2260 (1992); 115 4497,
9925, 11446 (1993); 117 10239 (1995)
- (PhO)₂POCl, Et₃N/DMAp JOC 47 1612 (1982)
-  JACS 104 6818 (1982); 110 8129 (1988)



Angew Int 16 876 (1977)

TL 21 4611 (1980)



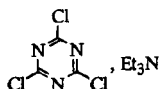
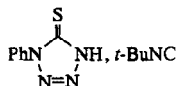
TL 2455 (1976); 2371 (1978); 2633 (1979); 21 4611 (1980); 25 2163 (1984); 32 517, 2719, 2723, 5781 (1991); 33 4213, 4931 (1992); 34 5385 (1993); 35 4409, 8237 (1994)

Syn 1 (1981) (review)

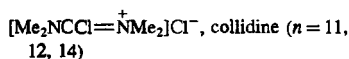
JOC 51 4840 (1986); 59 5414 (1994)

JACS 109 6176 (1987); 111 3973 (1989)
(polymer-supported diazodicarboxylate)

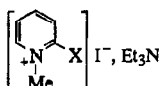
Angew Int 20 771 (1981)



TL 21 1893 (1980); 27 2369 (1986)



CL 1891 (1982)



X = Cl

CL 49 (1976); 441, 763, 959 (1977)

Angew Int 20 286 (1981)

JOC 51 3247, 4836 (1986)

JACS 108 2105 (1986); 109 8117 (1987); 110 6210 (1988); 112 1626, 5583 (1990)

TL 28 3031, 5759, 5763 (1987)

CC 1220 (1987)

SL 36 (1989); 328 (1990)

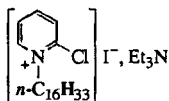
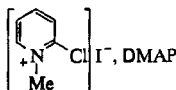
JACS 109 5437 (1987)

X = Br

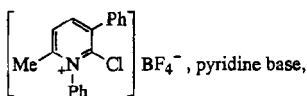
JOC 54 4268 (1989)

JACS 111 790 (1989)

TL 32 1649 (1991)



JOC 59 415 (1994)

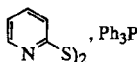
(PhCH₂NEt₃)Cl

CL 885 (1978)

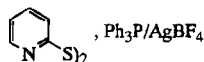


TL 2875 (1979)

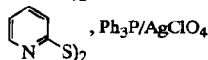
JACS 102 7583 (1980)



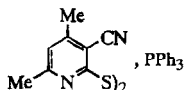
JACS 96 5614 (1974); 97 653, 654, 2287 (1975); 98 222 (1976); 103 3213 (1981); 104 1774 (1982); 108 6800 (1986); 112 3696 (1990); 113 6639 (1991)



TL 3405 (1976); 21 2791 (1980); 27 1815 (1986); 28
4993 (1987)
SL 367 (1993)

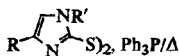


JACS 116 5511 (1994)

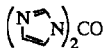


JOC 56 5132 (1991)

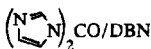
Angew Int 18 308 (1979)
Syn 986 (1986)



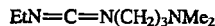
TL 3409 (1976)
JACS 100 4621 (1978); 101 7131 (1979); 106 2735
(1984)



TL 30 4181 (1989)



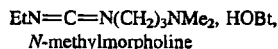
CC 1031 (1972)
JCS Perkin I 1718 (1976)



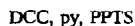
TL 29 37 (1988)



TL 32 4631 (1991)



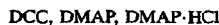
TL 35 201 (1994)



JACS 112 7407 (1990)



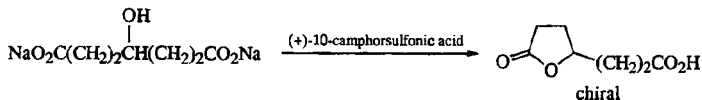
JACS 108 2776 (1986)
JOC 54 736, 896 (1989)



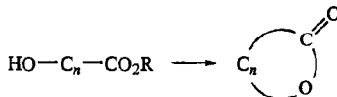
JOC 50 2394 (1985); 56 6606 (1991)
TL 29 1461 (1988); 34 5385 (1993)



TL 29 4225 (1988)



JACS 107 6404 (1985)
TL 27 5381 (1986)

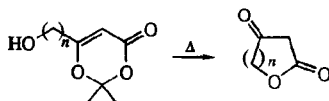


TL 28 805 (1987)

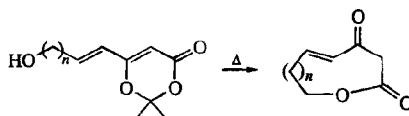


TL 28 805, 3861, 5367 (1987); 33 5681 (1992)
JOC 54 4263 (1989); 55 3546 (1990); 56 4050
(1991); 58 7535 (1993)

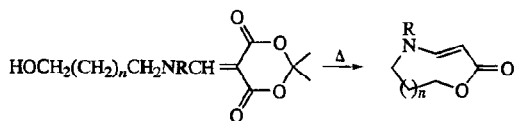
pig liver esterase (enantioselective)	JOC 56 4050 (1991)
<i>Pseudomonas fluorescens</i> (enantioselective)	Tetr Asym 2 733 (1991) (review)
imidazole	JACS 109 2208 (1987)
$\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$, Ph_3P	JACS 99 646 (1977)
$\text{NaO}-t\text{-Am}$	JOC 33 4176 (1968)
$\text{KO}-t\text{-Bu}$	JOC 57 2888 (1992)
KH	JACS 104 4015 (1982); 108 2662 (1986)
$n\text{-BuLi}$ ($\text{R} = \text{CH}_2\text{SO}_2\text{CH}_3$)	CL 455 (1982) JACS 106 2954 (1984)
H^+	Houben-Weyl, Vol VI/2 (1963), p 511 (review)
HF , H_2O	JOC 59 4122 (1994)
$\text{CF}_3\text{CO}_2\text{H}$	JOC 57 2888, 5036 (1992) SL 105 (1994)
$p\text{-TsOH}$	TL 33 5681 (1992) JOC 57 5947 (1992); 58 7304 (1993); 59 7849 (1994)
PPTS	JOC 55 2776 (1990)
Tf_2O , 2,6-di- <i>t</i> -butyl-4-methylpyridine	TL 33 5681 (1992)
$n\text{-Bu}_3\text{SnCl}$ ($\text{R} = \text{CH}_2\text{CF}_3$)	TL 34 3515 (1993)
$n\text{-Bu}_3\text{SnOMe}$ ($\text{R} = \text{CH}_2\text{CF}_3$)	TL 34 3515 (1993)
$(n\text{-Bu}_3\text{Sn})_2\text{O}$ ($\text{R} = \text{CH}_2\text{CF}_3$)	TL 34 3515 (1993)
$(n\text{-Bu}_3\text{Sn})_2$ ($\text{R} = \text{CH}_2\text{CF}_3$)	TL 34 3515 (1993)
$n\text{-Bu}_3\text{SnH}$ ($\text{R} = \text{CH}_2\text{CF}_3$)	TL 34 3515 (1993)
$\text{HOBu}_2\text{SnOSnBu}_2\text{Cl}$	TL 33 4957 (1992)
$\text{HOBu}_2\text{SnOSnBu}_2\text{SCN}$	TL 29 6689 (1988)
ZnCl_2 , molecular sieves	CC 1797 (1987)



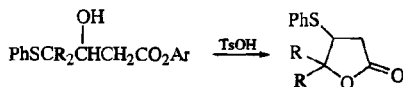
JOC 58 5011 (1993)



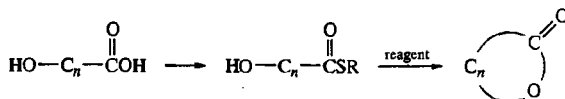
JACS 111 8286 (1989)



TL 35 1545 (1994)



TL 29 5321 (1988); 34 6783 (1993)

**Reagent**KO-*t*-BuTL 1469 (1979)
JOC 45 1535 (1980); 46 3209 (1981)
CC 251 (1982)CuO₂CCF₃

CC 1805 (1985) (dimerization)

AgClO₄Helv 57 2661 (1974); 58 2036 (1975); 59 755 (1976)
Org Syn 63 192 (1984)
Org Syn Coll Vol 7 470 (1990)
JOC 56 5132 (1991)AgBF₄Helv 57 2661 (1974)
JACS 116 5511 (1994)

AgOTf

JOC 56 5132 (1991)

AgO₂CCF₃

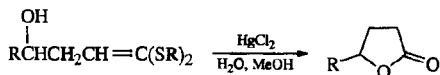
JACS 99 6756 (1977); 109 6205 (1987)

Hg(OMs)₂JACS 98 7874 (1976)
JOC 58 7932 (1993)Hg(OTf)₂

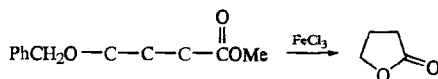
JOC 58 7768 (1993)

Hg(O₂CCF₃)₂

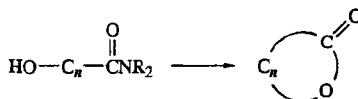
JACS 97 3513, 3515 (1975)



JOC 59 6018 (1994)



JOC 59 5532 (1994)



buffer

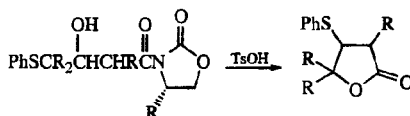
JOC 53 5130 (1988); 55 5867 (1990)

KOH

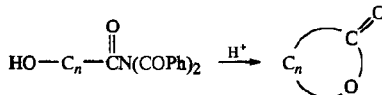
JOC 55 5433 (1990)



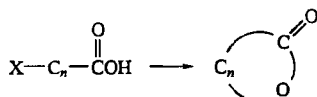
TL 31 1981 (1990)



TL 34 6783 (1993)



TL 33 7207 (1992)



Review: Acct Chem Res 14 95 (1981)

NaH (X = Br)

JOC 31 4043 (1966)

NaHCO₃ (X = OMs)

JOC 60 8318 (1995)

KHCO₃, (polymer-PBu₃)OMs, H₂O, toluene
(X = OMs)

JACS 104 2064 (1982)

K₂CO₃ (X = Br, I)

Ber 80 129 (1947)

Gazz Chim Ital 105 367 (1975)

Org Syn Coll Vol 6 698 (1988)

JOC 56 5132 (1991)

Cs₂CO₃ (X = Br, I)

CC 286 (1979); 251 (1982)

JACS 103 5183 (1981)

JOC 56 3045, 5132 (1991)


Cs₂CO₃ (X = OMs)

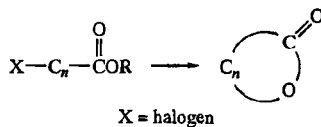
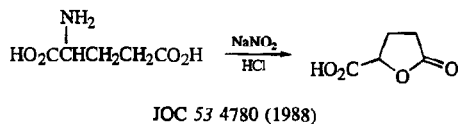
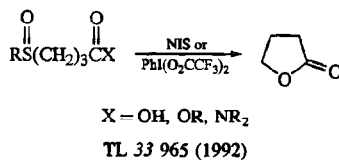
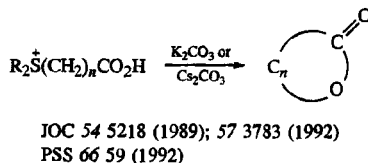
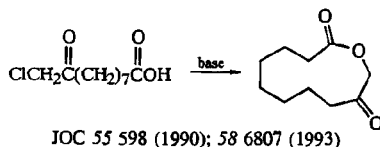
CC 668 (1982)

NaOH (X = Cl, Br)

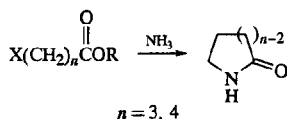
JACS 95 8374 (1973); 99 2591 (1977)

JOC 54 2364 (1989)

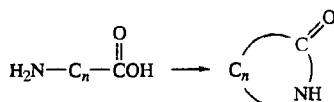
KOH (X = Br)	CC 251 (1982)
KOH, microemulsion (X = Br)	JOC 46 2594 (1981)
KOH, <i>n</i> -Bu ₄ NBr (phase transfer) (X = Br)	JOC 48 1533 (1983)
(<i>n</i> -Bu ₄ N)OH, CsClO ₄ (X = Br)	JOC 56 3045 (1991)
 (X = Br)	JOC 51 546 (1986)
Ag ₂ O (X = Br)	JOC 31 4043 (1966)



Δ (<i>n</i> = 3)	Bull Soc Chim Belg 87 215 (1973) JOC 50 2128 (1985) (phthalide)
Δ, silica gel (<i>n</i> = 3)	CL 1909 (1982) JOC 51 4944 (1986)
TsOH, Hg(OAc) ₂ or AgClO ₄ (<i>n</i> = 3)	Heterocycles 12 699 (1979)



JOC 54 3422 (1989)

 $(\text{CF}_3\text{CO})_2\text{O}$, DMAP

TL 36 6713 (1995)

MsCl, NaHCO_3

TL 32 2299 (1991)

MsCl, KHCO_3 , cat (*n*-Bu₄N)HSO₄, H₂O, HCCl₃

CL 443 (1981)

 $(n\text{-Bu}_4\text{N})\text{OH}/2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{SO}_2\text{Cl}$, *i*-Pr₂NEt

JACS 100 2916 (1978); 102 6613 (1980)

JOC 55 6000 (1990)

 $\text{SOCl}_2/\text{Et}_3\text{N}$

Heterocycles 14 1077 (1980)

JACS 117 928 (1995)

 $\text{SOCl}_2/\text{PhNMe}_2$

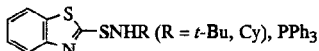
JOC 23 1102 (1958)

 $\text{SOCl}_2/\text{CH}_2\text{N}_2$

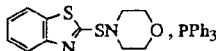
JOC 23 1102 (1958)

 $\sigma\text{-NO}_2\text{C}_6\text{H}_4\text{SCN}$, *n*-Bu₃P

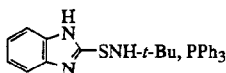
JOC 44 2945 (1979)



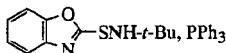
TL 36 3703 (1995)



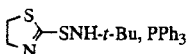
TL 36 3703 (1995)



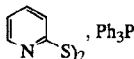
TL 36 3703 (1995)



TL 36 3703 (1995)



TL 36 3703 (1995)



JACS 103 2406 (1981)

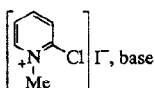
TL 26 1523 (1985); 27 2149, 2153 (1986); 28 4335 (1987); 29 1409 (1988); 33 943 (1992)

 $(\text{Me}_3\text{Si})_2\text{NH}$, Δ

Syn 614 (1978)

py, Δ

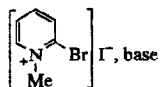
SL 531 (1992)



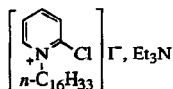
CL 1465 (1984)

JACS 111 1073, 1157 (1989); 112 2998 (1990); 115 7906 (1993)

TL 35 5113 (1994)



TL 31 2161 (1990)



IOC 59 415 (1994)

DCC

TL 21 2783 (1980); 31 3209 (1990)
JACS 112 6255 (1990)EtN=C=N(CH₂)₃NMe₂, DMAP, DMAP·HCl

TL 33 1725 (1992)

EtN=C=N(CH₂)₃NMe₂, HOBT

TL 33 1725 (1992)

Ph₂P(O)OC₆F₅

IOC 59 5192 (1994)

Ph₂POCl, Et₃N

CC 1242 (1988)

PhPOCl₂, Et₃N

TL 31 2905 (1990)

PhOPOCl₂, Et₃NTL 31 2905 (1990)
JOC 56 2244 (1991)EtOPOCl₂, Et₃N

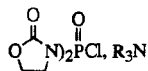
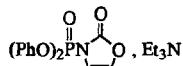
TL 31 2905 (1990)

(PhO)₂POCl, Et₃N

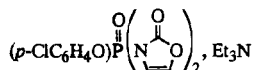
JOC 56 2244 (1991)

Me₂NPOCl₂, Et₃N

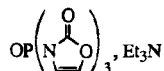
JOC 56 2244 (1991)

(PhO)₂PON₃, baseJOC 44 3101 (1979); 52 764 (1987); 55 6000 (1990)
CC 344 (1986)
TL 30 5061 (1989); 31 2021 (1990); 35 591 (1994)
JACS 112 7659 (1990); 115 3420 (1993)
SL 250 (1994)Syn 547 (1980)
CC 378 (1989)
JCS Perkin I 47 (1990)
JOC 57 1067 (1992); 58 471 (1993); 59 4712 (1994)
JACS 115 8451 (1993)

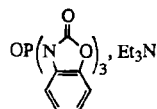
TL 29 2203 (1988)

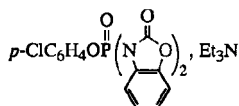


TL 29 2203 (1988)



TL 29 2203 (1988)

Chem Pharm Bull 36 1249 (1988)
TL 36 8693 (1995)



Chem Pharm Bull 36 1249 (1988)

CB, py

JOC 43 4393 (1978)

alumina or silica gel

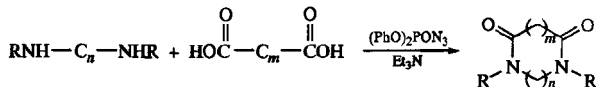
TL 21 2443 (1980)

n-Bu₂SnO

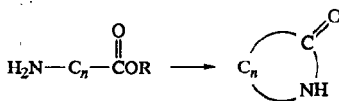
JACS 102 7578 (1980); 105 7130 (1983); 117 9768 (1995)

Ti(O-*i*-Pr)₄

TL 29 3049 (1988)



TL 31 6469 (1990)



Δ

JOC 22 830 (1957); 58 3840 (1993)
TL 36 373 (1995)

NaOH

TL 35 281 (1994)

NaOH / (PhO)₂PON₃, Et₃N

CC 344 (1986)

KO-*t*-Bu

JOC 55 2694 (1990)

DMAP

SL 63 (1993)

(PhO)₂PON₃, NaHCO₃

TL 34 5385 (1993)

MeMgI

JOC 23 1102 (1958); 59 2497 (1994)
Ann 639 157 (1961); 2195 (1975)
JACS 102 2060 (1980)

EtMgBr

Bull Soc Chim Belg 32 412 (1923)
Ann 2195 (1975)
JOC 60 143 (1995)*t*-BuMgCl

TL 28 5481 (1987); 32 5287 (1991)

PhMgBr

SL 239 (1993)

Me₃Al

TL 36 5227 (1996)

Et₃Al

JACS 111 6228 (1989)

i-Bu₃Al

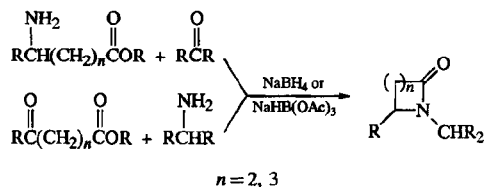
JACS 88 852 (1966)

Sn[N(SiMe₃)₂]₂ / Me₃CCO₂H or MeCONH-*t*-Bu

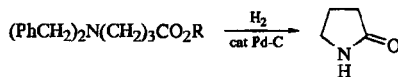
JACS 115 9417 (1993) (β-lactams)

porcine pancreatic lipase

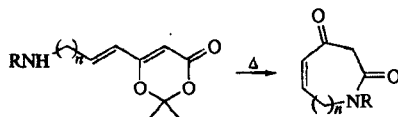
TL 33 3943 (1992)



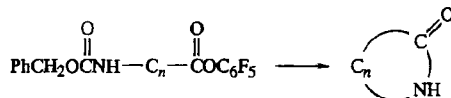
SL 81 (1994)



JOC 58 52 (1992)



JACS 112 9292 (1990)

ReagentsH₂, cat Pd-C

JOC 47 3261 (1982); 55 6000 (1990); 59 2314 (1994)

TL 30 7021 (1989)

HCl/K₂CO₃

JOC 55 6000 (1990)

HCl/N-methylmorpholine

JOC 58 5592 (1993)

CF₃CO₂H/K₂CO₃

Syn 236 (1987)

TL 33 4799 (1992)

CF₃CO₂H/DMAP, Na₂HPO₄

TL 35 565 (1994)

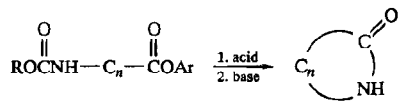
Me₃SiOTf/base

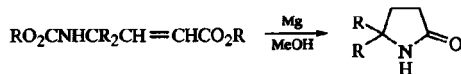
Syn 236 (1987)

TL 29 3057, 3227 (1988)

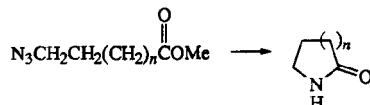
Me₃SiClO₄/K₂CO₃

Syn 236 (1987)

JOC 43 296 (1978) (Ar = 2,4,5-Cl₃C₆H₂)JACS 100 8202 (1978) (Ar = p-NO₂C₆H₄)



TL 34 4439 (1993)

Reagent(s)nPPh₃, H₂O

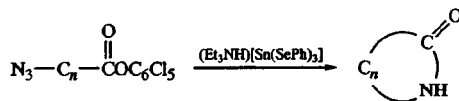
1

TL 35 6417 (1994)

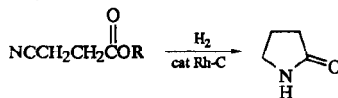
n-Bu₃P, HCl

2

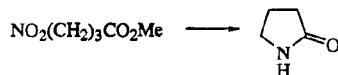
JOC 59 7038 (1994)



JOC 56 5132 (1991)



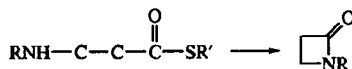
JOC 54 3422 (1989)

H₂, cat Pd/C

J Med Chem 30 498 (1987)

NaBH₄, cat NiCl₂·6H₂O, ultrasound

JOC 55 3088 (1990)

*t*-BuMgCl

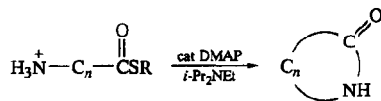
TL 32 5287 (1991)

CuOTf

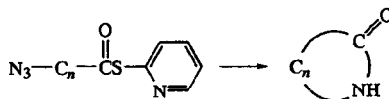
JOC 54 3511 (1989)

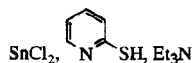
Hg(O₂CCF₃)₂

CL 915 (1986)



TL 35 5547 (1994)





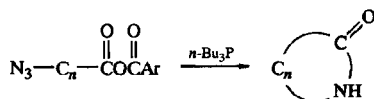
TL 33 3669 (1992)



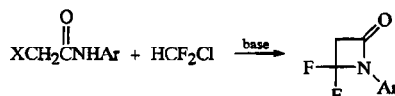
JOC 56 5132 (1991)



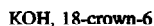
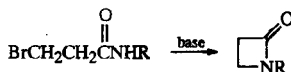
JOC 56 5132 (1991)



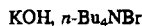
TL 34 4671 (1993)



JOC 58 245 (1993)



JOC 53 4339 (1988)

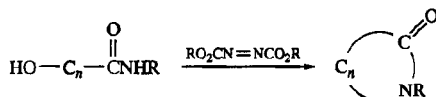


TL 31 1755 (1990)



JOC 23 1102 (1958)

TL 31 1759 (1990)

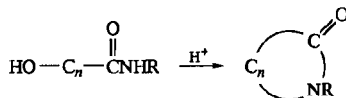
 \underline{n}

2

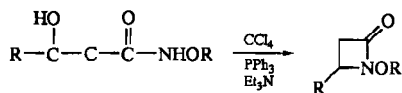
JOC 46 1229 (1981); 58 618 (1993)
 JACS 111 1073 (1989); 112 760 (1990)
 TL 31 4317 (1990)

3

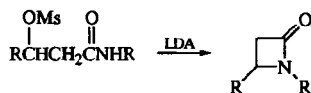
JOC 58 860, 2334 (1993)



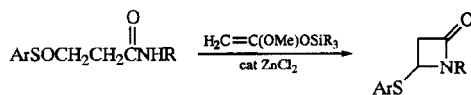
JOC 57 70 (1992)



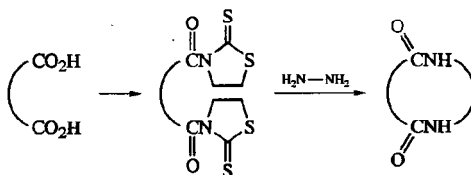
JOC 59 4862 (1994)



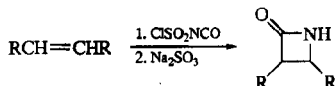
JOC 60 6176 (1995)



TL 36 115 (1995)



CL 159 (1980)



JACS 88 3657 (1966) (allenes)

Angew Int 7 3657 (1968) (review)

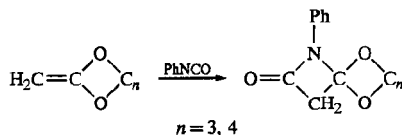
JOC 33 3036 (1968) (alkenes and allenes); 35 2043 (1970); 36 2841 (1971) (dienes)

TL 3823 (1968) (dienes); 30 5631 (1989); 32 2265 (1991)

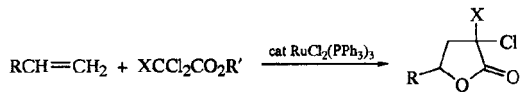
Ann 539 (1974)

Org Syn Coll Vol 8 3 (1993)

SL 539 (1994)

 $n = 3, 4$

TL 29 2327 (1988)



X = H, Cl, Me

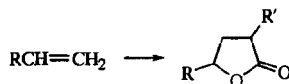
R'

H

CL 363 (1978)

SiMe₃

CL 1011 (1979)



$p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{Cl}$, $\text{ZnCl}_2/\text{NaOCl}$, cat RuCl_3
($\text{R}' = \text{H}$)

TL 29 6925 (1988)

$\text{R}'\text{CHBrCO}_2\text{H}$, $(\text{PhCO}_2)_2$

CL 415 (1981)

$\text{R}'\text{CH}_2\text{CO}_2\text{H}$, $\text{Mn}(\text{OAc})_3 \cdot 2\text{H}_2\text{O}$

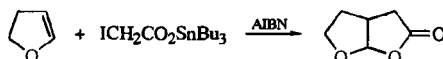
JACS 90 5903, 5905 (1968); 96 7977 (1974); 106 5384 (1984) (3-oxo-6-alkenoic acids); 115 8871 (1993) ($\text{R}' = \text{CN}$)
BCSJ 49 1041 (1976)
Org Syn 61 22 (1983)
TL 26 3761 (intramolecular; $\text{R}' = \text{CN}$, CO_2H), 4921 ($\text{R}' = \text{CN}$, CO_2Et) (1985); 32 1011 (1991); 35 2903 (1994) ($\text{R}' = \text{H}$, CO_2Me)
JOC 50 10, 1026 ($\text{R}' = \text{CO}_2\text{H}$, spiro lactones), 3143 (1985)
Tetr 42 3429 (1986) (mechanism)
Org Syn Coll Vol 7 400 (1990)

$\text{MeO}_2\text{CCH}_2\text{CO}_2\text{H}$, CAN, ultrasound ($\text{R}' = \text{CO}_2\text{Me}$)

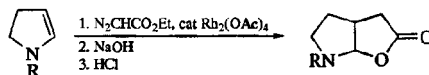
TL 35 2083 (1994)

$\text{RCH}(\text{CO}_2\text{R})_2$, $\text{Fe}(\text{ClO}_4)_3 \cdot 9\text{H}_2\text{O}$ ($\text{R}' = \text{CO}_2\text{R}$)

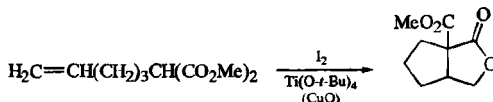
SL 42 (1990)



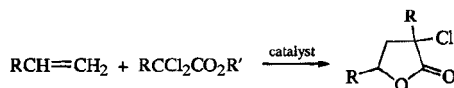
TL 25 3939 (1984); 27 3715, 5927 (1986)
Tetr 41 4039 (1985)



TL 35 1425 (1994)



TL 33 2167 (1992); 35 1059 (1994); 36 1479 (1995) (chiral catalyst)
JOC 58 3106 (1993)



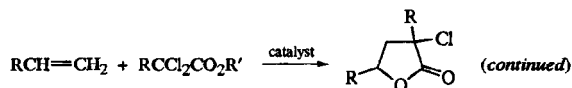
R'

Catalyst

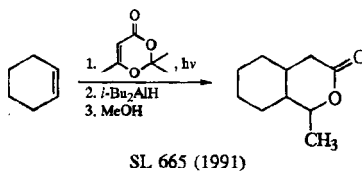
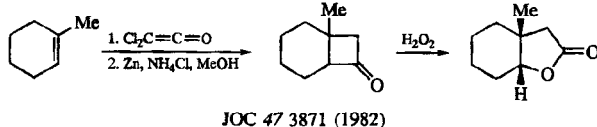
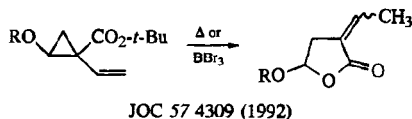
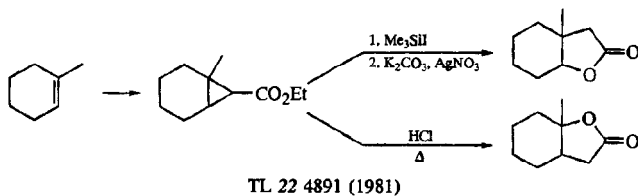
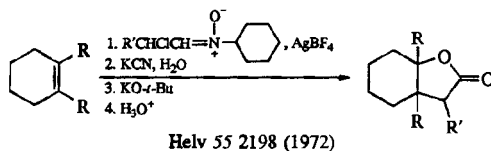
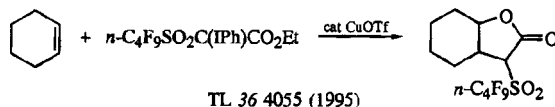
H

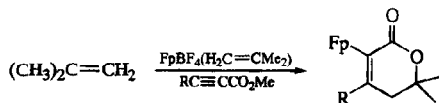
$\text{FeCl}_2[\text{P}(\text{OEt})_3]_3$
 $\text{RuCl}_2(\text{PPh}_3)_3$

JOC 51 5501 (1986) (intramolecular)
CC 363 (1978)
JOC 51 5501 (1986) (intramolecular)



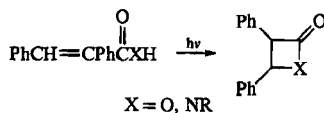
R'	Catalyst	
Me	[CpMo(CO) ₃] ₂ [CpFe(CO) ₂] ₂	Tetr 28 29 (1972) Tetr 28 29 (1972)
alkyl	FeCl ₂ [P(OEt) ₃] ₃ RuCl ₂ (PPh ₃) ₃	JOC 51 5501 (1986) (intramolecular) JOC 51 5501 (1986) (intramolecular)
SiMe ₃	RuCl ₂ (PPh ₃) ₃	CC 1011 (1979)





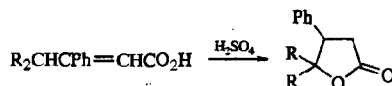
$\text{R} = \text{H}, \text{Me}; \text{Fp} = \text{CpFe}(\text{CO})_2$

Organomet 1 397 (1982)

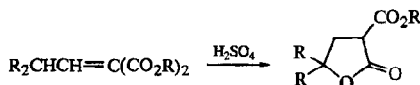


$\text{X} = \text{O}, \text{NR}$

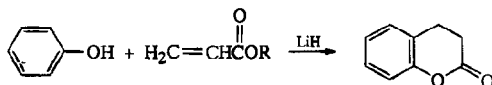
JACS 89 4243 (1968)



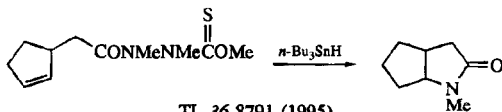
Acta Chem Scand B 36 371 (1982)



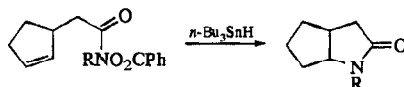
Syn Commun 11 35 (1981)



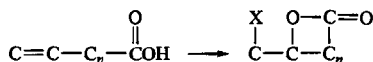
TL 33 1161 (1992)



TL 36 8791 (1995)



TL 35 6109 (1994)



Reviews:

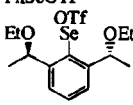
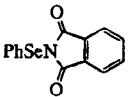
Russ Chem Rev 40 272 (1971) ($\text{X} = \text{halogen}$)

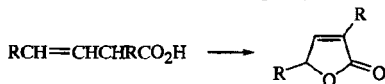
Chem Soc Rev 8 171 (1979) ($\text{X} = \text{halogen}$)

Tetr 37 4097 (1981) ($\text{X} = \text{SePh}$)

P. A. Bartlett, "Asymmetric Synthesis," Ed. J. D. Morrison, Academic Press, New York (1984), Vol 3, Part B, Chpt 6

<u>X</u>	<u>Reagent(s)</u>	
H	h ν , Ph-Ph, 1-C ₁₀ H ₇ CN	JACS 109 7547 (1987); 113 9870 (1991)
Cl	Cl ₂	Gazz Chim Ital 81 305 (1951) Tetr 4 393 (1958)
	TsNClNa	JOC 46 3552 (1981)
Br	Br ₂	Tetr 4 393 (1958) JOC 60 5093 (1995)
	Br ₂ (on NaO ₂ CR)	TL 2595 (1971)
	Br ₂ , NaHCO ₃	JOC 55 2487 (1990) TL 36 1205 (1995)
	Br ₂ (on TiO ₂ CR)	TL 335 (1979)
	Br ₂ , TiO ₂ CCMe ₃	CC 1044 (1987)
	NBS	TL 3983 (1967); 1005 (1977) (chiral); 21 2733 (1980); 27 6079 (1986); 28 2801 (1987) Tetr 30 819 (1974); 35 2337, 2345 (1979) CL 1109 (1977) (chiral) JOC 52 1372 (1987); 53 640 (1988)
I	I ₂ , (base)	JOC 38 800 (1973); 44 1625 (1979); 51 2505, 4840 (1986); 52 3346 (1987); 53 3210 (1988); 55 6236 (1990); 56 353, 3572 (1991); 57 33 (1992); 58 3840 (1993); 59 1898, 3389 (1994) TL 2543 (1977); 335 (1979); 22 4611 (1981); 27 6079 (1987); 29 1517, 4865 (1988); 33 6505 (1992); 34 7081 (1993) JACS 100 3950 (1978); 102 2118 (1980); 103 4114 (1981); 105 5819 (1983); 108 5559 (1986); 109 6844 (1987); 111 2596, 3712, 7507 (1989) Tetr 40 2317 (1984) Org Syn 64 175 (1985) Org Syn Coll Vol 7 164 (1990)
	I ₂ (on TiO ₂ CR)	JCS Perkin I 1864 (1974)
	I ₂ , TiOAc	Austral J Chem 32 2793 (1979)
	I ₂ , KI	JACS 76 2315 (1954); 91 5675 (1969); 92 397 (1970); 106 7854 (1984); 109 6389 (1987) Proc Acad Sci USSR, Chem Sec 146 787 (1962) TL 1777 (1972); 2543 (1977); 27 3297, 5467 (1986); 31 6235 (1990) CC 472 (1972) Tetr 30 819 (1974) CL 351 (1982) JOC 51 4600, 4944 (1986); 52 4399 (1987); 53 3195 (1988); 55 1169 (1990); 57 4664, 7133 (1992)
	I ₂ , pyridine base	JOC 57 33 (1992)
	NIS	JOC 55 2409 (1990)
	I(sym-collidine) ₂ PF ₆	TL 34 4527, 5723 (1993) JOC 58 4 (1993); 59 5912 (1994)
	KI, Na ₂ S ₂ O ₈ , NaHCO ₃	SL 899 (1993)
OH	m-ClC ₆ H ₄ CO ₃ H	TL 28 2045 (1987)
OTs	PhI(OH)OTs	TL 27 4557 (1986)

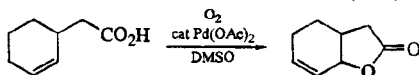
$O_2P(OPh)_2$	$PhI(OH)O_2P(OPh)_2$	JACS 110 2987 (1988)
SMe	$(MeSSMe_2)BF_4$, $i-Pr_2NEt$	TL 26 6159 (1985)
SAr	$PhSCl$, R_3N	CC 293 (1977) JACS 101 3884 (1979) TL 28 523 (1987) JOC 57 4025 (1992)
SeAr	$(ArS)_2$, $(NH_4)_2S_2O_8$, CF_3SO_3H	JOC 57 4025 (1992)
	$PhSeCl$	CC 484 (1977) JACS 99 3185 (1977); 101 3884 (1979); 103 4114 (1981); 106 6060 (1984); 111 7507 (1989) TL 4801 (1979); 24 4769 (1983); 29 4625, 4865 (1988); 31 2235 (1990) Tetr 36 1399 (1980); 37 4097 (1981) (review); 40 2317 (1984) JOC 51 3023 (1986); 57 5778 (1992)
	ArSeX (X = Cl, Br)	Ber 93 317 (1960)
	$PhSeOTf$	CL 849 (1987)
		JOC 60 4660 (1995)
	$PhSeOTs$	JOC 56 2781 (1991)
		Tetr 40 2317 (1984)
	$(PhSe)_2$, electrolysis	TL 28 6511 (1987)
	$(PhSe)_2$, $h\nu$	JOC 57 4019 (1992)
TeAr	$ArTeI$	Ber 93 317 (1960)
$TeCl_2Ar$	$ArTeCl_3$	TL (6) 11 (1959) Ber 93 317 (1960) Tetr 18 521 (1962) Syn Commun 13 889 (1983)
HgX	HgX_2 (X = Cl, OAc)	Tetr 40 2317 (1984) R. C. Larock, "Solvomercuration/Demercuration Reactions in Organic Synthesis," Springer, New York (1986), Chpt 5 (review)



Br_2 , $NaHCO_3$ / $AgNO_3$, $HOAc$ TL 34 1411 (1993)

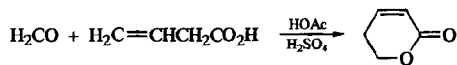
$(NH_4)_2S_2O_8$, cat $(PhSe)_2$ SL 798 (1993)

Na_2CO_3 / Li_2PdCl_4 BCSJ 50 1899 (1977)



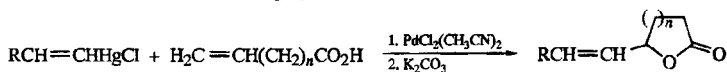
JOC 58 5298 (1993)

TL 34 8545 (1993)

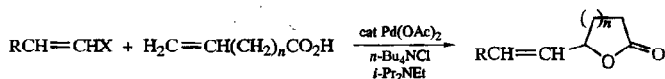


Syn 510 (1974)

Org Syn Coll Vol 6 462 (1988)

 $n = 1, 2$

TL 28 4977 (1987)

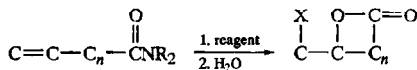
 $\text{X} = \text{Br}, \text{I}, \text{OTf}; n = 1, 2$

TL 29 6399 (1988)

SL 748 (1994) (3,4-dihydroisocoumarins)



<u>X</u>	<u>Y</u>	<u>Reagent</u>	
Cl, Br, I	OMe	X ₂	JOC 45 839 (1980)
Br	OMe	Br ₂	JOC 58 2946 (1993)
OH	OEt	<i>m</i> -ClC ₆ H ₄ CO ₃ H	TL 28 2045 (1987)
SPh	OMe	PhSCl	JOC 45 839 (1980)
SePh	OSiMe ₂ (<i>t</i> -Bu)	PhSeCl	JACS 107 1448 (1985)
	OMe	PhSeCl	JOC 45 839 (1980)
		PhSeOTf	CC 849 (1987)
HgX (X = Cl, OAc)	OR	HgX ₂	R. C. Larock, "Solvomercuration / Demercuration Reactions in Organic Synthesis," Springer Verlag, New York (1986), Chpt 6 (review)

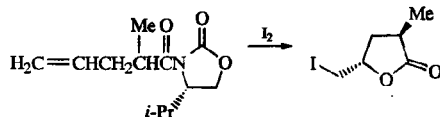


<u>X</u>	<u>Reagent</u>	
Cl	NCS	JACS 106 1079 (1984)
Br	NBS	JACS 106 1079 (1984)
		TL 30 3845 (1989)
		JOC 54 1178 (1989)

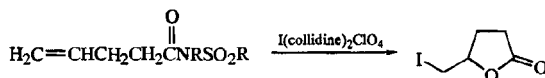
- I I₂ TL 1625 (1977); 31 3175 (1990); 34 2165 (1993); 35 4123, 8915 (1994)
 JACS 106 1079 (1984); 109 6716 (1987); 111 4829 (1989); 117 11106 (1995)
 CC 156 (1986)
 JOC 53 4282 (1988); 54 1178 (1989); 55 6236, 6241 (1990); 57 6088 (1992); 59 6504, 7201 (1994)

- OH *m*-ClC₆H₄CO₃H BCSJ 58 3309 (1985)
 TL 28 2041, 2045 (1987)
 CC 445 (1989)
 JOC 59 7201 (1994)

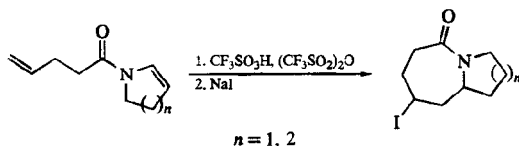
- SePh PhSeCl JOC 55 863 (1990)



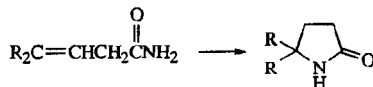
JOC 59 6504 (1994)



TL 33 6999 (1992)



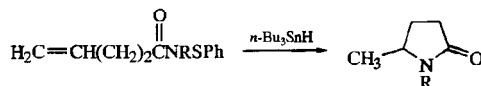
$n = 1, 2$
 TL 35 393 (1994)



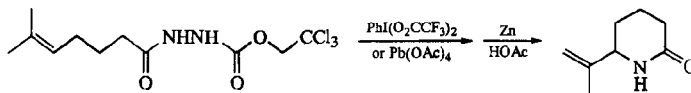
- PPA JOC 22 830 (1957)
 J Heterocyclic Chem 4 143 (1967)

- P₂O₅, CH₃SO₃H JOC 50 2220 (1985)

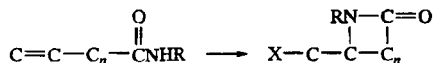
- CF₃SO₃H TL 35 293 (1994)



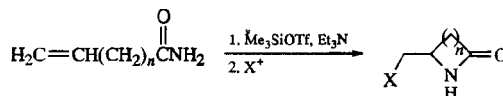
TL 34 6877 (1993)



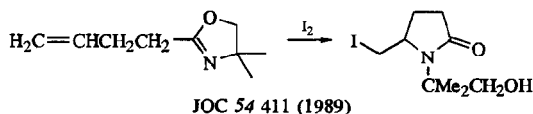
TL 33 5717 (1992)



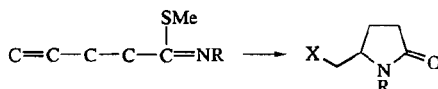
<u>X</u>	<u>Reagent(s)</u>	<u>n</u>	
Br	Br ₂	1	JOC 52 4471 (1987) TL 28 6257 (1987) (both R = OCO ₂ CH ₂ Ph) TL 26 5385 (1985) (R = O ₂ CR') TL 30 2045 (1989)
	Br ₂ , K ₂ CO ₃	1	
	NBS	2	TL 30 2045 (1989)
Br, I	X ₂ , HCO ₃ ⁻	1	JACS 104 3233 (1982) (R = SO ₂ R')
I	Me ₃ SiOTf, Et ₃ N / I ₂	2, 3	TL 26 1803 (1985) JOC 53 4006 (1988) Org Syn 70 101 (1991) JOC 60 4428 (1995)
	NIS, NaOH	2, 3	
SPh	PhSCl/base	0 (β-lactam formation)	JACS 105 7345 (1983)
SePh	PhSeX (X = Cl, Br, I)	2, 3	JOC 51 1724 (1986); 52 2018 (1987)
HgOAc	Hg(OAc) ₂	2, 3	TL 4993 (1979); 24 11, 15, 2051 (1983) JOC 44 330 (1979); 46 3920 (1981)



<u>X⁺</u>	<u>n</u>	
Br(collidine) ₂ ClO ₄	2, 3	JOC 53 4773 (1988)
I ₂	1-3	TL 26 1803 (1985) JOC 53 4006 (1988)



JOC 54 411 (1989)

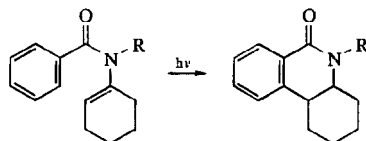


<u>X</u>	<u>Reagent</u>	
Br	Br(collidine) ₂ ClO ₄	Heterocycles 26 359 (1987)

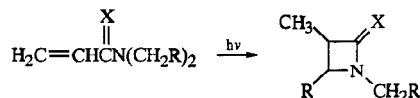
1

I₂

CC 1627 (1987)
 JOC 54 4812 (1989); 55 3792,
 3947 (1990)



"The Alkaloids," Vol XXII, Ed. A. Brossi, Academic Press, New York (1983), p 189
 SL 547 (1995)

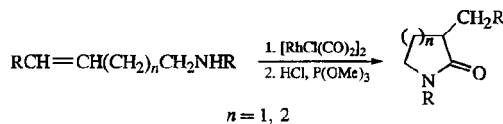
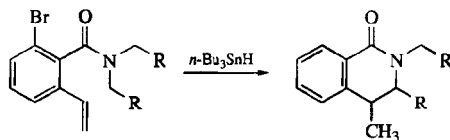
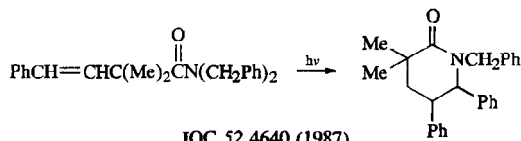
X

O

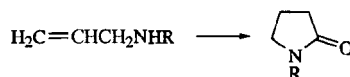
Tetr 33 485 (1977)
 JOC 57 3490 (1992)

S

CC 1214 (1990)



Organomet 7 2528 (1988)
 TL 29 6421 (1989); 30 539 (1989)
 JACS 114 9215 (1992)

CO, cat Rh(BPh₄)(COD), NaBH₄, *i*-PrOH

JOC 57 3328 (1992)

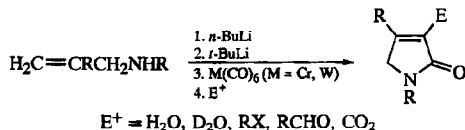
CO, cat HRh(CO)(PPh₃)₃, NaBH₄, *i*-PrOH

JOC 57 3328 (1992)

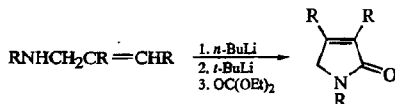
CO, H₂, cat Rh(BPh₄)(COD), cat [Ru(CO)₃Cl₂]₂ JOC 57 3328 (1992)

CO, H₂, cat Rh₄(CO)₁₂ J Mol Catal 63 335 (1990)

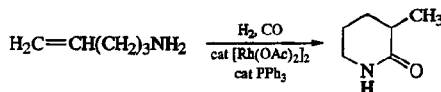
CO, cat ClRh(PPh₃)₃ or RhCl(CO)(PPh₃)₂ JOMC 188 223 (1980)



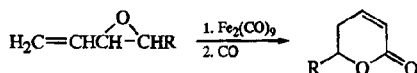
TL 34 7777 (1993)



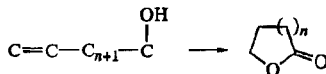
TL 29 4859 (1988)



TL 31 4795 (1990)



SL 395, 399 (1992)



Reagent(s)

(bipyH₂)CrOCl₅

CrO₃, HOAc, Ac₂O

(*n*-C₁₆H₃₃NMe₃)MnO₄

n

1, 2

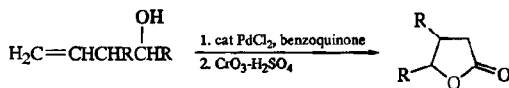
1, 2

1, 2

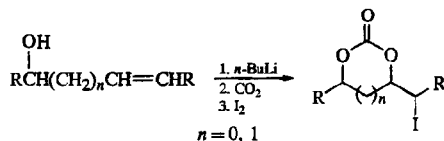
CL 551 (1985)

TL 26 127 (1985)

TL 27 4079 (1986)



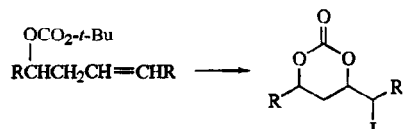
TL 29 5181 (1988)



CC 465 (1981)

JOC 47 4013, 4626 (1982); 49 1147 (1984); 53 4495 (1988); 58 5666 (1993)

TL 35 6263 (1994)



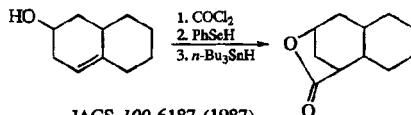
IBI

TL 33 6439 (1992)

JOC 58 3703 (1993)

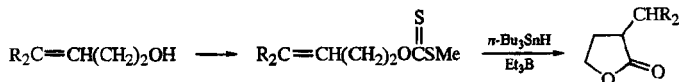


JOC 47 4013 (1982)

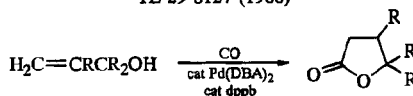


JACS 109 6187 (1987)

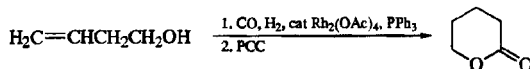
JOC 57 4696 (1992); 58 6857 (1993)



TL 29 6127 (1988)

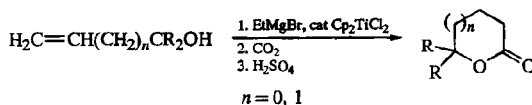


JOC 56 5357 (1991)

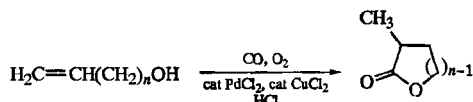


TL 25 4051 (1984)

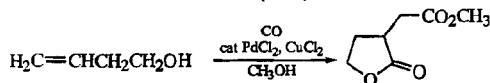
JACS 113 5337 (1991)

 $n = 0, 1$

JOMC 160 C8 (1978)

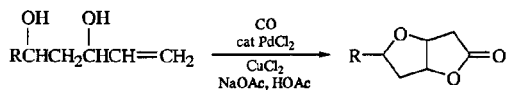
 $n = 2, 3$

CC 511 (1985)



TL 28 325 (1987)

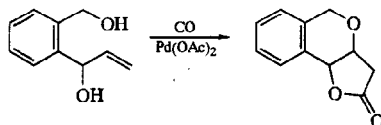
JOC 56 1099 (1991)



TL 26 3207 (1985)

Syn 1108 (1991)

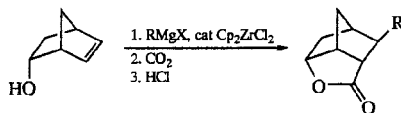
SL 191 (1992)



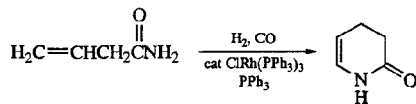
TL 25 3171 (1984)

JACS 115 5859 (1993)

JOC 60 1154 (1995)

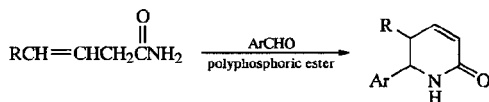


JACS 114 6692 (1992)

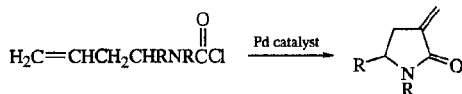


TL 30 6283 (1989)

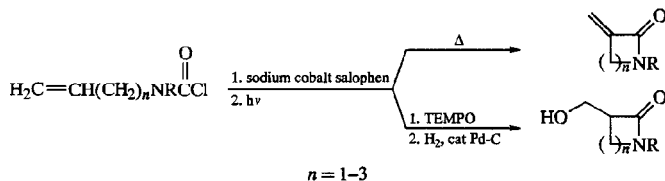
JOC 56 2024 (1991)



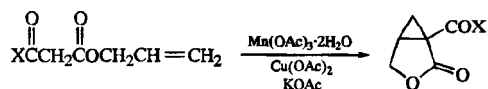
JOC 57 5045 (1992)



TL 27 6339 (1986)

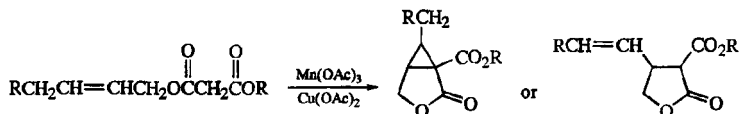


TL 30 3229 (1989); 32 259 (1991)

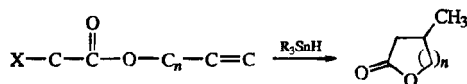


X = R, OR

TL 30 331 (1989)



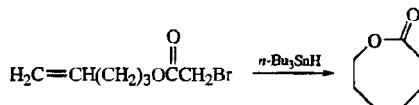
JOC 54 5684 (1989)

 $n = 1, 2$; X = Cl, Br, I; R = *n*-Bu, Ph

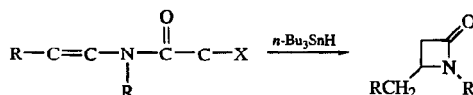
CC 1438 (1987)

TL 30 4363 (1989)

JOC 55 3436 (1990)



JACS 114 10981 (1992)



X = Cl, Br

TL 32 2335 (1991)

JCS Perkin I 2399 (1992)

SL 649 (1993); 445 (1994); 912, 915 (1995)

JOC 60 1276 (1995)

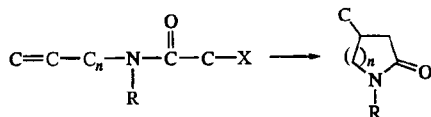


X = Cl, Br, SPh

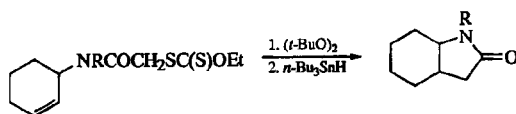
TL 32 1725 (1991)

JCS Perkin I 2399 (1992)

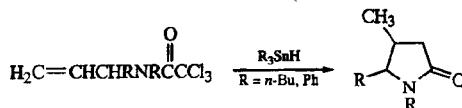
JOC 60 8044 (1995)



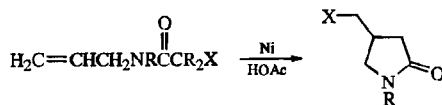
Reagent	<i>n</i>	<i>X</i>	
<i>n</i> -Bu ₃ SnH	1	Cl	JCS Perkin I 879 (1989) JOC 56 95 (1991) SL 871 (1993)
		Br	Heterocycles 28 723 (1989)
		SPh	JCS Perkin I 879 (1989)
	2, 3	Cl	JCS Perkin I 353 (1991)
(Me ₃ Si) ₃ SiH	1	Cl	SL 871 (1993)



TL 35 1719 (1994)

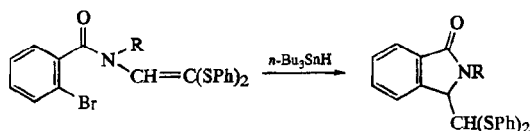


JOC 58 464 (1993)

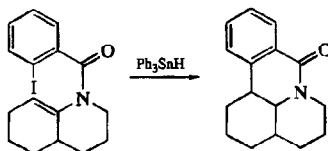


X = H, Cl, Br

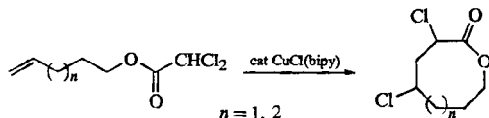
TL 35 5629 (1994)



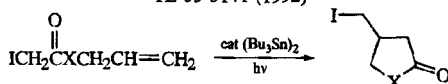
TL 36 6733 (1995)



JOC 60 8044 (1995)

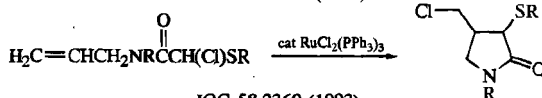


TL 33 5141 (1992)

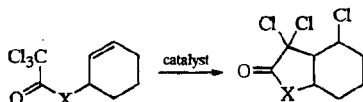
 $X = \text{O, NR}$

TL 31 1121 (1990)

JOC 56 2746 (1991)



JOC 58 2360 (1993)

Catalyst

CuCl

TL 24 2395 (1983)

Heterocycles 22 1779 (1984)

JOC 55 985 (1990)

SL 739 (1993)

CuCl(bipy)

CC 652 (1984); 518 (1985)

JOC 54 4497 (1989); 57 1682 (1992)

TL 34 6821 (1993)

CC 652 (1984); 518 (1985)

JOC 54 4497 (1989)

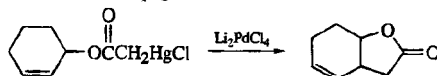
JOC 58 464 (1993)

CuCl

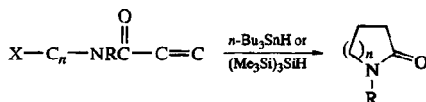
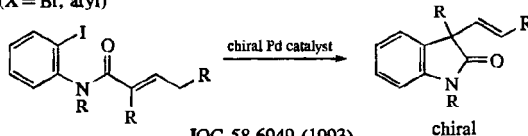
CuCl, bipy

 $\frac{X}{O}$

NR

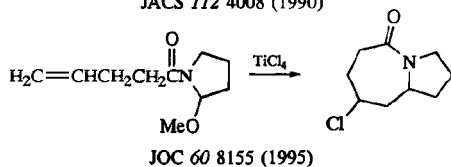
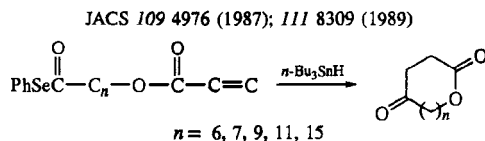
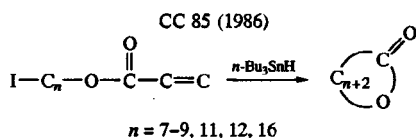
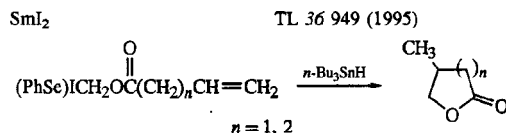
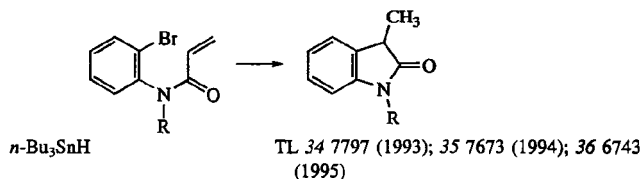
For intermolecular reactions of $X = \text{O}$, see page 1724, Section 2.

TL 30 2767 (1989); 31 17 (1990)

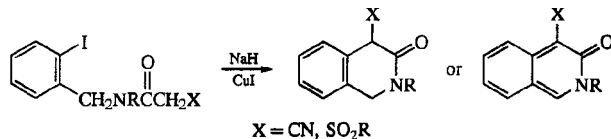
TL 30 2585 (1989) ($X = \text{Br, aryl}$); 35 4031 (1994) ($X = \text{I, } n = 3$); 36 625 (1995) ($X = \text{SePh, } n = 3$)SL 384 (1990) ($X = \text{Br, aryl}$)

JOC 58 6949 (1993)

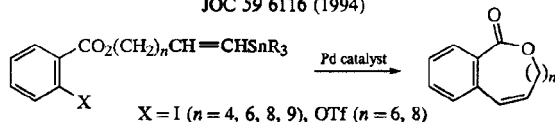
chiral



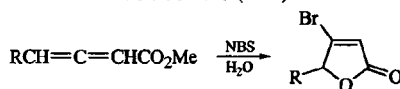
JOC 60 8155 (1995)



JOC 59 6116 (1994)

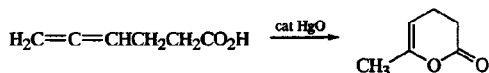


JOC 56 2883 (1991)

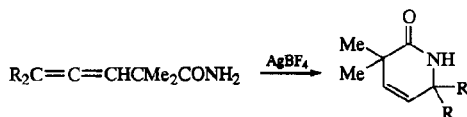


TL 31 5517 (1990)

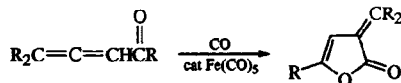
JOC 60 1814 (1995)



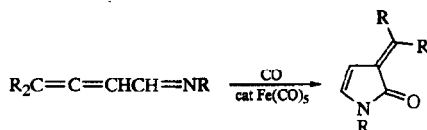
TL 25 3179 (1984)



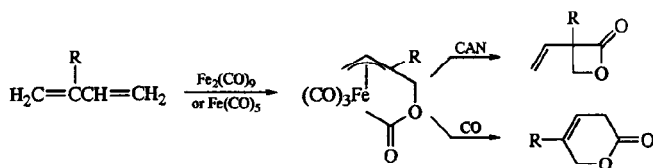
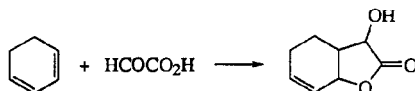
TL 27 5089 (1986)



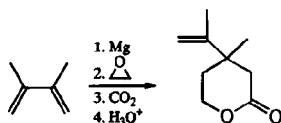
JACS 115 7545 (1993)

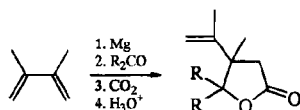


JOC 59 7488 (1994)

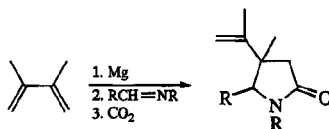
CC 581 (1977)
JCS Perkin I 270 (1981)Ber 112 3644 (1979)
SL 326, 331 (1990)See also JCS Perkin I 1355 (1982)
Tetr 40 1737 (1984)

TL 32 7529 (1991)

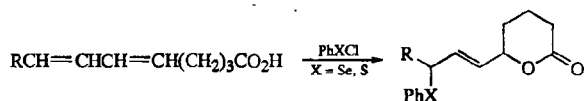
TL 34 6007 (1993)
JOC 60 5143 (1995)



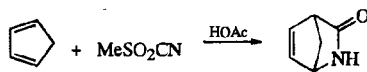
JOC 57 7007 (1992); 60 5143 (1995)



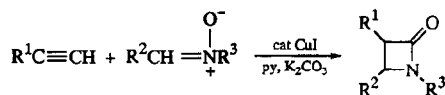
JOC 60 1077 (1995)



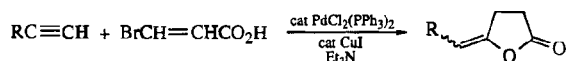
TL 27 5919 (1986)



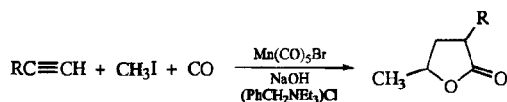
JOC 58 6129 (1993)



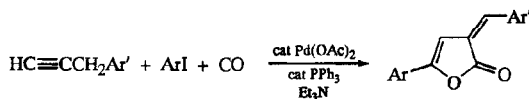
JOC 60 4999 (1995)



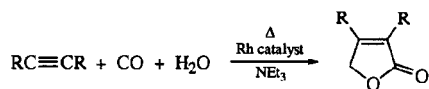
TL 34 5963 (1993)



JOC 51 273 (1986)

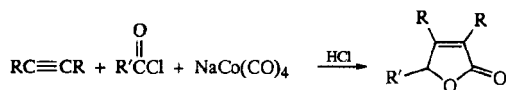


JOC 56 4534 (1991)

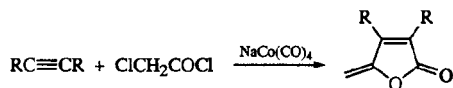


CC 649 (1987)

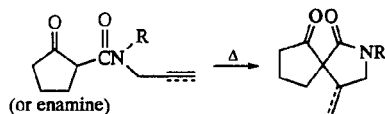
JOC 58 5386 (1993)



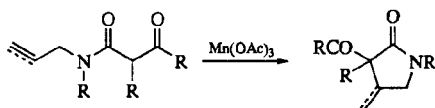
TL 31 5139 (1990)



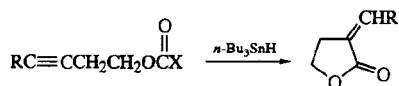
SL 865 (1991)



TL 33 2505 (1992)



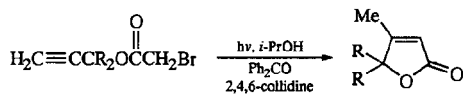
TL 30 4531 (1989)



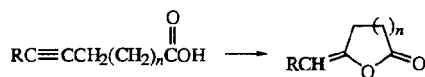
X = Cl, SePh

TL 27 641 (1986); 29 2581 (1988)

JOC 57 4696 (1992)



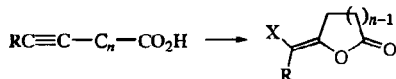
TL 31 7539 (1990)

 $n = 1, 2$

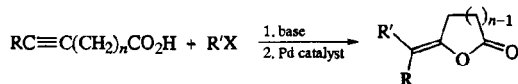
Catalyst

(Cy ₂ PCH ₂ CH ₂ PCy ₂) ₂ RhCl	JACS 109 6385 (1987)
Pd(PPh ₃) ₄	JACS 109 6385 (1987)
PdCl ₂ (PhCN) ₂	TL 25 5323 (1984)
Ag	SL 871 (1995)
AgI	SL 871 (1995)
Ag ₂ CO ₃	TL 28 6447 (1987); 35 3525 (1994)
AgNO ₃	JCS 3962 (1958) JOC 49 736 (1984)
HgO	JCS Perkin I 582 (1981) TL 25 3179 (1984)
Hg(OAc) ₂	JOC 43 560 (1978) JACS 103 5459 (1981)
Hg(O ₂ CCF ₃) ₂	JACS 103 4114 (1981); 108 5589 (1986) JOC 50 2331 (1985); 54 3963 (1989); 56 2624 (1991); 58 1900 (1993)
HCO ₃ ⁻	Acta Chem Scand 11 582 (1957) JCS 1313 (1958) JACS 103 4114 (1981)

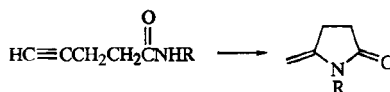
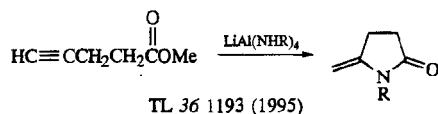
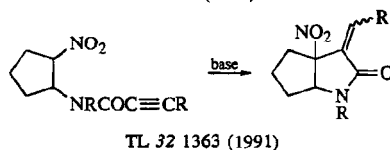
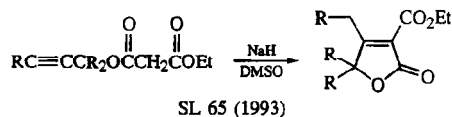
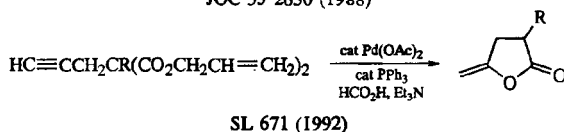
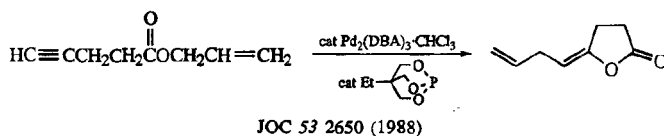
For intermolecular reactions, see page 1636, Section 5.



<u>X</u>	<u>Reagent(s)</u>	<u>n</u>	
Cl	NCS, KHCO ₃ , <i>n</i> -Bu ₄ NOH	2	JACS 103 5459 (1981)
Br	NBS, KHCO ₃ or K ₂ CO ₃	2, 3	J Biol Chem 258 15046 (1983) JOC 56 2624, 6893 (1991)
	NBS, KHCO ₃ , <i>n</i> -Bu ₄ NOH	2, 3	JACS 103 5459 (1981)
	NaOH / AgNO ₃ / Br ₂	2, 3	JOC 56 6893 (1991)
I	I ₂ , KHCO ₃	3	J Biol Chem 258 15046 (1983) JOC 50 2331 (1985)
	I ₂ , KI, buffer	2, 3	JOC 54 2764 (1989)
	NIS, NaHCO ₃	2	JACS 108 5589 (1986)
	NIS, KHCO ₃	2, 3	J Biol Chem 258 15046 (1983) JOC 50 2331 (1985)
	NIS, KHCO ₃ , <i>n</i> -Bu ₄ NOH	2, 3	JACS 103 5459 (1981)

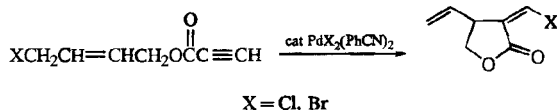


R^1X	n	
$ArBr(I)$	2	JOC 57 976 (1992)
$RCH=CHCH_2OAc$	2	JOC 53 2650 (1988)
$RCH=CHCH_2Cl$	2-4	JACS 108 2753 (1986)
$RCH=CHBr(OTf)$	2	JOC 57 976 (1992)
$RC\equiv CBr$	2	TL 33 2811 (1992); 34 3129 (1993)

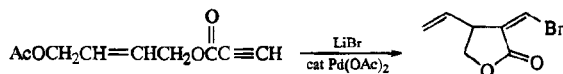


$n\text{-Bu}_4\text{NF}$ TL 33 6231, 6235 (1992); 36 1193, 1197, 2717 (1995)

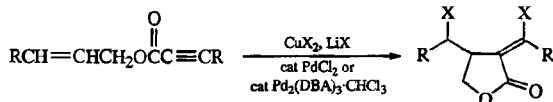
$\text{PdCl}_2(\text{MeCN})_2$ TL 33 6231 (1992)



JOC 56 5120 (1991); 58 3692 (1993)



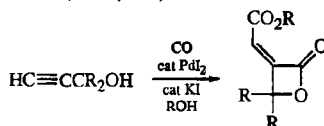
JOC 60 1087 (1995)



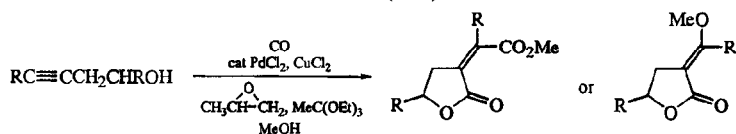
X = Cl, Br

JOC 58 1245 (1993); 60 1160 (1995)

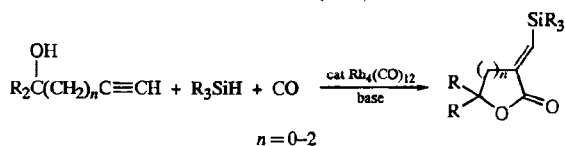
SL 68, 745 (1993)



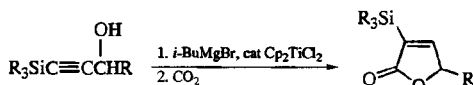
CC 1429 (1994)



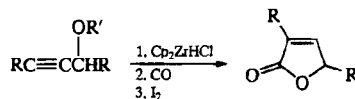
JOC 56 1099 (1991)



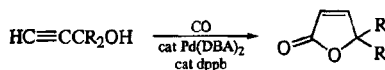
JACS 112 6120 (1990)



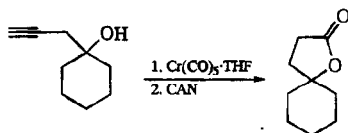
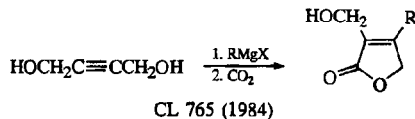
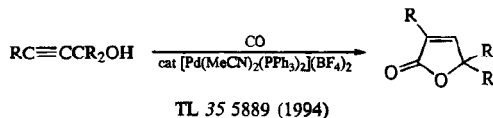
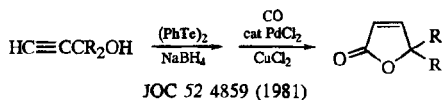
TL 31 6399 (1990); 34 4975 (1993)

R' = H, CH₂Ph, SiR₃

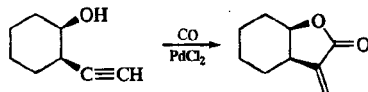
TL 29 3445 (1988)



JOC 56 5357 (1991)

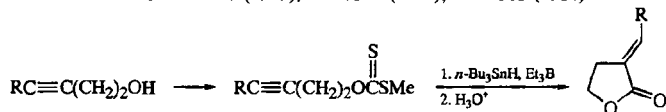


TL 35 3801, 8883 (1994); 36 8087 (1995)

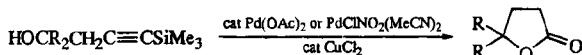


TL 51 (1975)

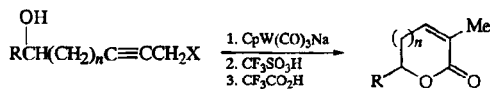
JACS 101 4107 (1979); 103 7520 (1981); 106 5505 (1984)



TL 29 6127 (1988)

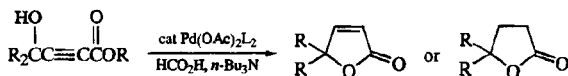


SL 943 (1994)

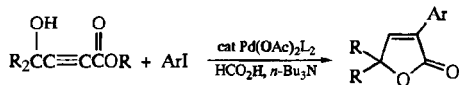


X = halogen, n = 0-2

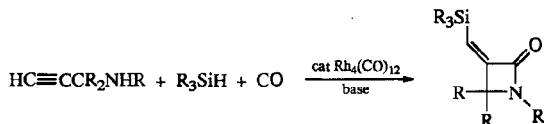
JACS 117 2933 (1995)



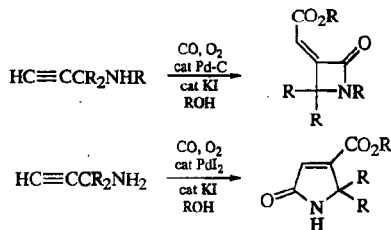
Tetr 44 481 (1988)



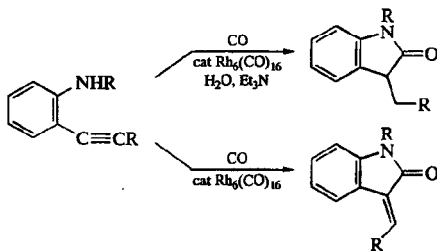
Tetr 44 481 (1988)



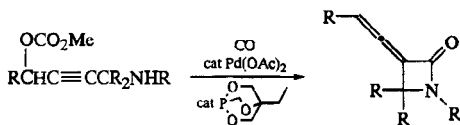
TL 32 7431 (1991)



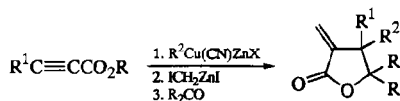
TL 36 7495 (1995)



TL 36 6243 (1995)

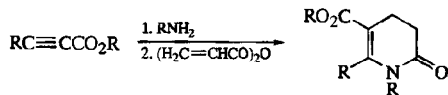


TL 32 7683 (1991)

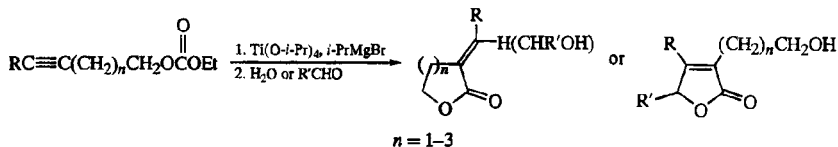


JACS 114 7579 (1992)

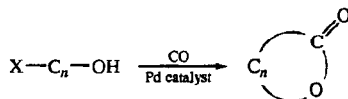
JOC 58 2694 (1993)



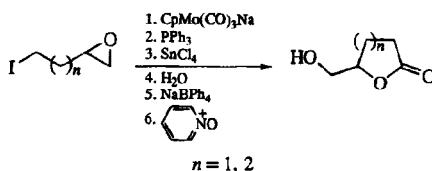
TL 35 1669 (1994)



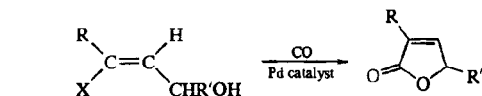
TL 36 6075 (1995)



JACS 102 4193 (1980)



TL 35 6717 (1994)



x

halogen

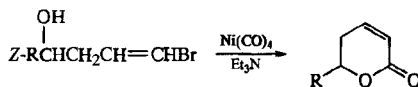
TL 133 (1979); 28 723 (1987); 35 695, 7517 (1994)

JACS 102 4193 (1980)

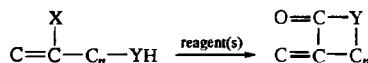
JOC 52 3860, 3883 (1987)

OTf

JOC 57 6972 (1992); 60 4845 (1995)



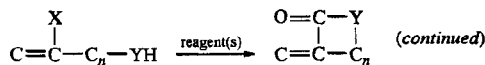
TL 24 3209 (1983)



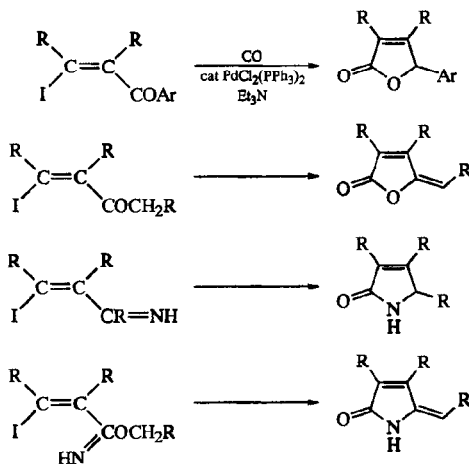
Reagent(s)

$$\text{Ni(CO)}_4, \text{KOAc}$$
CL 773 (1978) ($n=2$, $X=\text{Br}$, $Y=\text{O}$)
$$\text{Ni(CO)}_4 \text{ or } \text{Ni(CO)}_2(\text{PPh}_3)_2$$

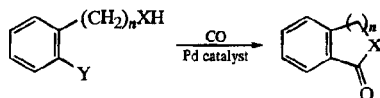
JOC 46 1723 (1981) ($n = 2, 3$; $X = \text{Br}$; $Y = \text{O}$)

Reagent(s)Ni(CO)₂PPh₃JACS 104 6879 (1982) (*n* = 2; X = Br; Y = O)TL 32 6749 (1991) (*n* = 2; X = Br; Y = O)

CO, Pd catalyst

JOC 47 3630 (1982) (*n* = 2, X = Br, Y = O); 48 4058(1983) (*n* = 2-4; X = Br, I; Y = O, NH)TL 29 5601 (1988) (*n* = 1, X = Br; Y = NH)

JACS 117 3422 (1995)

X = O, NR; Y = Br, I, OTf; *n* = 1-3

Heterocycles 6 1711, 1841 (1977); 12 921 (1979); 16 1491 (1981)

JOC 43 1684 (1978); 57 6972 (1992); 59 7164 (1994)

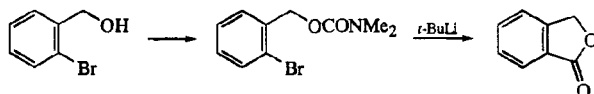
JACS 102 4193 (1980)

Syn Commun 10 523 (1980)

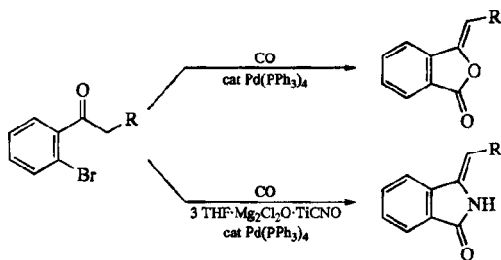
Chem Pharm Bull 32 3840 (1982)

CC 841 (1986)

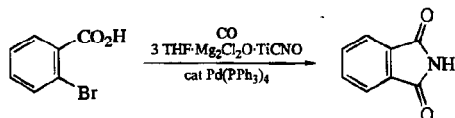
SL 245 (1994)



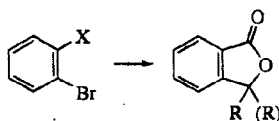
JOC 57 2029 (1992)



JACS 111 3725 (1989)



JACS 111 3725 (1989)

XReagentsCO₂H2 *n*-BuLi / R₂CO or RCHO / H₃O⁺

JOC 41 2628 (1976)

CO₂-*i*-Pr*n*-BuLi / R₂CO or RCHO / H₃O⁺

JOC 41 2704 (1976)

Mg / R₂CO or RCHO / H₃O⁺

JOC 39 2787 (1974)

XnReagents

O

1

Fe₂(CO)₉ / CAN

TL 32 2651 (1991)

2

CO, cat Co₂(CO)₈

JOC 54 20 (1989)

CO, cat Co₂(CO)₈, cat Ru₃(CO)₁₂

JOC 54 20 (1989)

NR

1

CO, cat [Rh(CO)₂Cl]₂

JACS 105 6737 (1983); 111 931 (1989)

CO, Ni(CO)₄, LiI

CC 710 (1988)

JOC 55 2943 (1990)

2

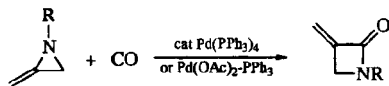
CO, cat Co₂(CO)₈

JACS 111 7539 (1989)

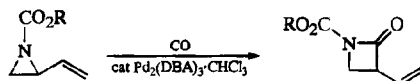
3

CO, cat Co₂(CO)₈, cat Ru₃(CO)₁₂

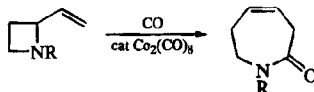
JACS 114 7018 (1992)



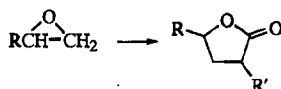
TL 28 3237 (1987)



SL 91 (1991)



JACS 111 7539 (1989)

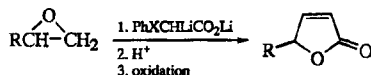


JOC 39 2783 (1974)

R'CHLiNCONMe₂/acid ion exchange resin

Ber 108 48 (1975)

See also the reaction of epoxides with alpha metallated carboxylic acids and derivatives on page 1717, Section 5.



X

S

CL 385 (1974)

BCSJ 50 242 (1977)

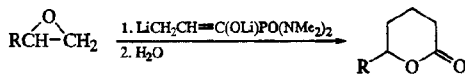
TL 26 5627 (1985)

Se

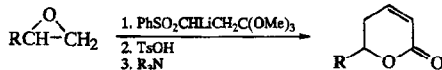
CC 754 (1986)

TL 28 1147 (1987)

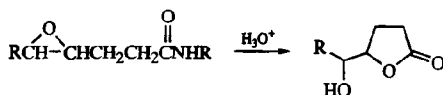
JOC 55 5766 (1990)



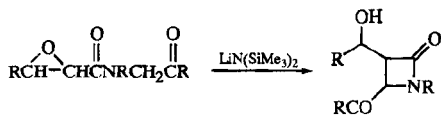
TL 47 (1976)



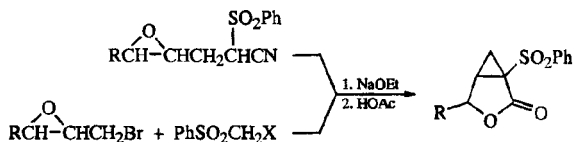
TL 29 2059 (1988)



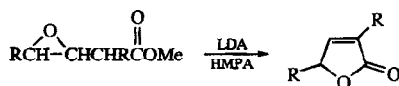
JOC 57 6696 (1992)



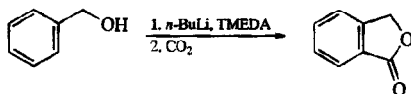
JOC 53 450 (1988)

X = CO₂Et, CN

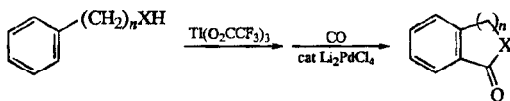
TL 34 6443 (1993)



TL 31 6789 (1990)

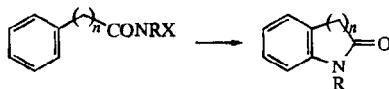


JOC 45 1835 (1980); 59 4043 (1994)

X = O (n = 1, 2); CO₂ (n = 0, 1); CONH (n = 0)

JOC 45 363 (1980)

JACS 104 1900 (1982)

XReagent(s)n

Cl

Ag₂CO₃, CF₃CO₂H

1-3

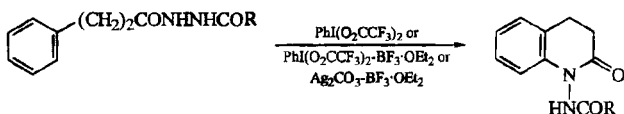
JOC 54 3394 (1989) (R = OMe)

OAc

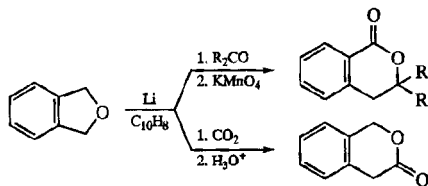
FeCl₃

1, 2

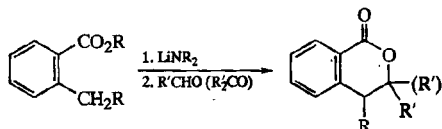
TL 30 715 (1989) (R = H)



TL 35 2043 (1994)



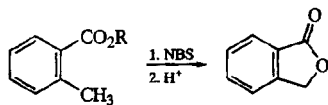
TL 36 8123 (1995)



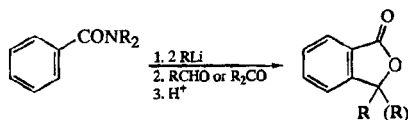
CC 764 (1983) (chiral); 520 (1987)

JCS Perkin I 1043 (1984)

TL 33 3359, 7569 (1992)



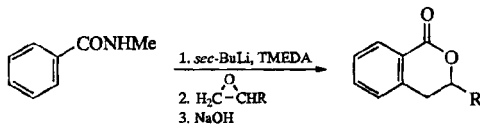
JOC 52 183 (1987)



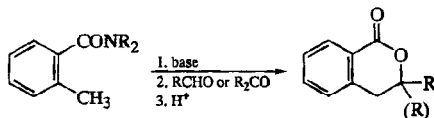
JOC 29 853 (1964); 51 3566 (1986)

TL 32 3845 (1991)

For other ortho lithiation reactions, see page 88, Section 2.1.



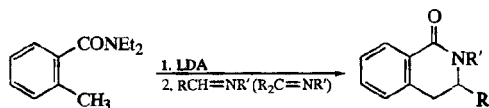
TL 35 3949 (1994)



JOC 29 3514 (1964); 51 3566 (1986)

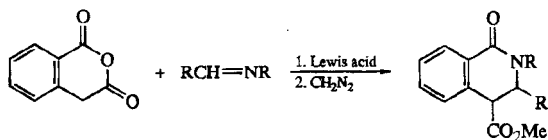
J Heterocyclic Chem 6 83 (1969)

TL 633 (1970)

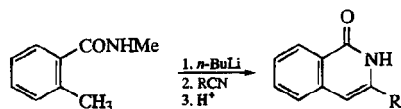


Heterocycles 23 825 (1985)

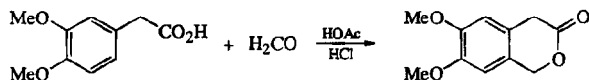
JOC 52 5378 (1987); 53 2378 (1988); 54 1174, 2992 (1989)



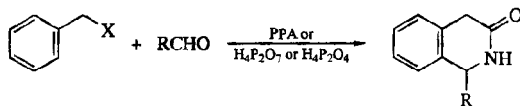
TL 31 193 (1990)



JOC 47 3787 (1982)



Org Syn Coll Vol 6 471 (1988)

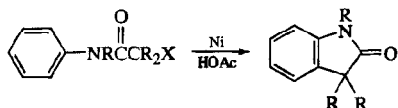


X = CONH2, CN

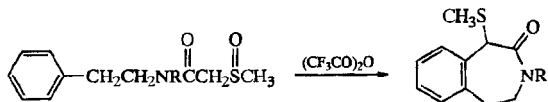
Syn 393 (1975)

Heterocycles 26 2385 (1987)

TL 36 3969 (1995)

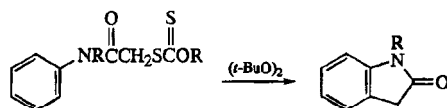


TL 35 9553 (1994)

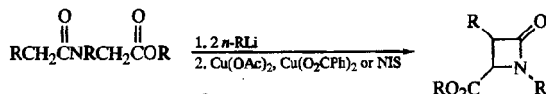


Chem Pharm Bull 37 939 (1989)

SL 49 (1994)

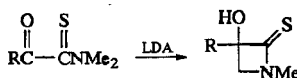


TL 35 1719 (1994)

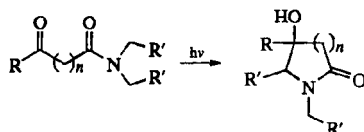


JACS 111 6843 (1989)

JOC 57 1864 (1992)



JACS 117 5859 (1995)

 $\frac{n}{0}$

0

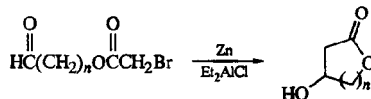
TL 371 (1969); 1103 (1973)

JACS 101 5343 (1979); 105 1958 (1983)

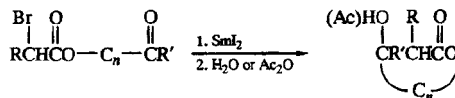
1

CC 743 (1974)

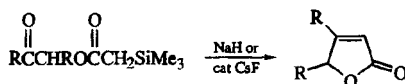
JOC 43 1005 (1978)

 $n = 9, 11, 12$

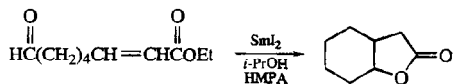
JACS 99 7705 (1977)



See page 1125, Section 2.1.

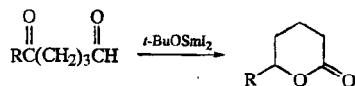


JOC 55 1108 (1990)

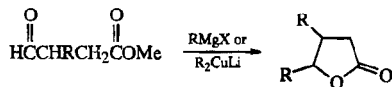


TL 33 7899 (1992)

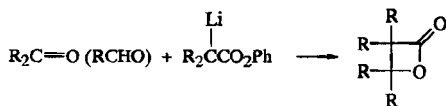
JOC 58 6266 (1993)



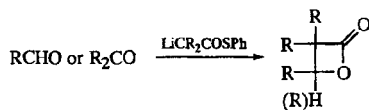
TL 32 5097 (1991)



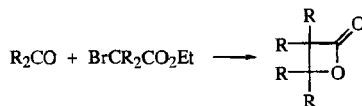
JOC 58 6280 (1993)



JOC 60 758 (1995)



JOC 56 1176 (1991); 58 322 (1993)



electrolysis

Angew Int 32 1191 (1993)

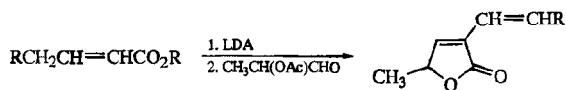
JOC 59 3161 (1994)

In

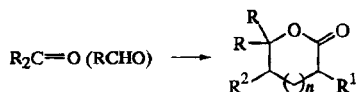
JOC 59 3161 (1994)





Zn

JOC 59 3161 (1994)



TL 36 7515 (1995)



<i>n</i>	Reagents	
0	H ₂ C=CHMgBr/H ₂ O/EtMgBr, cat Cp ₂ TiCl ₂ /CO ₂ /H ⁺ (R ¹ =R ² =H)	JOMC 160 C8 (1978)
	LiCH ₂ CMe ₂ CH ₂ OSiR ₃ / <i>n</i> -Bu ₄ NF/ cat (<i>n</i> -Pr ₄ N)RuO ₄ , NMO (R ¹ =Me ₂ , R ² =H)	TL 32 3215 (1991)
	Li(CH ₂) ₃ OCH(OEt)CH ₃ /H ₃ O ⁺ /CrO ₃ , H ⁺ or py (R ¹ =R ² =H)	JOC 37 1947 (1972) TL 4651 (1976)
	Li(CH ₂) ₂ CH(OEt) ₂ /NH ₄ Cl, H ₂ O/ <i>m</i> - ClC ₆ H ₃ CO ₂ H, BF ₃ ·OEt ₂ (R ¹ =R ² =H)	CC 1534 (1987)
	LiCH ₂ CH=C(OEt)N ⁺ (N ₂)N ⁻ /H ₃ O ⁺  (R ¹ =R ² =H)	JOC 60 6, 7597 (1995)
	ClMg(CH ₂) ₃ OMgCl/PCC (R ¹ =R ² =H)	SL 207 (1994)
	BrMg(CH ₂) ₂  /Ac ₂ O/NaOH/H ₃ O ⁺ / H ₂ CrO ₄ (R ¹ =R ² =H)	Syn Commun 7 27 (1977)
	Li(CH ₂) ₂ CO ₂ Li/TsOH (R ¹ =R ² =H)	TL 883 (1978)
	H ₂ C=CHCH ₂ MgBr/H ₂ O/BH ₃ /H ₂ O ₂ , OH ⁻ /H ₂ CrO ₄ (R ¹ =R ² =H)	BSCF 3377 (1973) JOC 42 1623 (1977)
	LiCH ₂ CH=CHSiMe ₃ /CH ₃ CO ₂ H, H ₂ SO ₄ (R ¹ =R ² =H)	CC 772 (1977)
	LiCH ₂ CH=CHSiMe ₃ / <i>t</i> -BuO ₂ H, cat VO(acac) ₂ /MeOH, BF ₃ ·OEt ₂ /CrO ₃ , H ₂ SO ₄ (R ¹ =R ² =H)	TL 21 11 (1980) JACS 102 5004 (1980)
	LiCH ₂ CH=C(OLi)PO(NMe ₂) ₂ /H ₂ O (R ¹ =R ² =H)	TL 47 (1976)
	Li or NaC≡CCH(OEt) ₂ /H ₂ , cat Pd-C/ H ₂ CrO ₄ (R ¹ =R ² =H)	JOC 22 570 (1957) JACS 86 485 (1964)
	 , TiCl ₄ /TsOH (R ¹ =R ² =H)	JACS 99 7360 (1977); 108 3745 (1986)
	 /H ⁺ /NaOH, H ₂ O ₂ or NaOBr or HOCl (R ¹ =R ² =H)	TL 887 (1972); 923 (1973) JACS 93 3773 (1971); 94 4777 (1972); 95 5321 (1973)
	CH ₃ CHLiCH=C(CN)NMe ₂ /H ₃ O ⁺ (R ¹ =H, R ² =Me)	TL 21 1205 (1980)
	CH ₃ CHLiCH=C(CN)OR/H ₃ O ⁺ (R ¹ =H, R ² =Me)	JOC 45 395 (1980)
	H ₂ C=CHCO ₂ Et, electrolysis (R ¹ =R ² =H)	Rec Trav Chim 93 47 (1974)
	R ² CH=CR ¹ CO ₂ CH ₃ , Me ₃ SiCl, electrolysis	TL 21 5029 (1980)
	ArCH=CHCO ₂ Et, Me ₃ SiCl, Mg (R ¹ =H, R ² =Ar)	JOC 60 458 (1995)
	H ₂ C=CHCO ₂ Me, Me ₃ SiCl, NaI, Sm (R ¹ =R ² =H)	JOC 59 7902 (1994)
	H ₂ C=CHCO ₂ Me, Me ₃ SiBr, Sm (R ¹ =R ² =H)	JOC 59 7902 (1994)

$R^2CH=CR^1CO_2Et$, SmI_2 , ROH, (HMPA)

CC 624 (1986); 920 (1987) (intramolecular)

TL 27 5763 (1986)

SL 207 (1994)

JOC 50 5907 (1985)

 $MeO_2CCH_2CH_2Sn(n-Bu)_3$, $TiCl_4$
 $(R^1 = R^2 = H)$
 $RO_2CCH_2CH_2TiCl_3$ ($R^1 = R^2 = H$)

JACS 108 3745 (1986)

 $RO_2CCH_2CH_2TiCl(O-i-Pr)_2$ ($R^1 = R^2 = H$)

JOC 60 4602 (1995)

 $RO_2CCH_2CH_2Br(I)$; Ce, La, Nd or Sm

CC 475 (1986)

 $(R^1 = R^2 = H)$

JOC 55 1628 (1990)

1

 $H_2C=CHCH_2MgBr/H_2O/EtMgBr$, cat


JOMC 160 C8 (1978)

 $Cp_2TiCl_2/CO_2/H^+$ ($R^1 = R^2 = H$)

 $H_2C=CH(CH_2)_2MgBr/H_2O/BH_3/H_2O_2$,

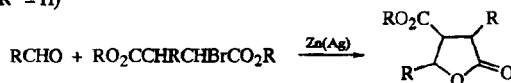
BSCF 3377 (1973)

 $NaOH/H_2CrO_4$ ($R^1 = R^2 = H$)

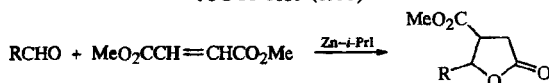

 $CH(CH_2)_3Li/H_3O^+/PCC$ or H_2CrO_4
 $(R^1 = R^2 = H)$

TL 31 3767 (1990)

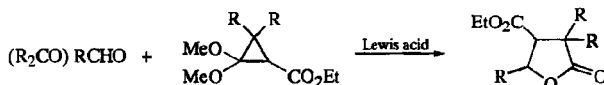
JOC 56 3825 (1991)



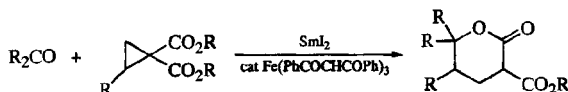
JOC 58 1159 (1993)



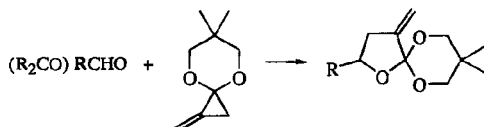
CL 1217 (1981)



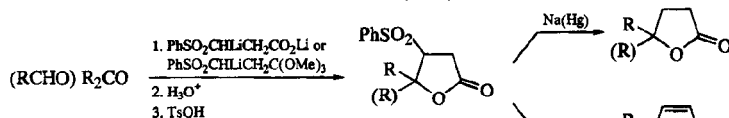
JOC 57 7126 (1992); 58 5226 (1993)



TL 35 7805 (1994)

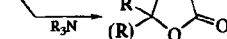
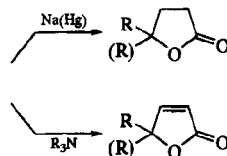


JOC 55 5553 (1990)



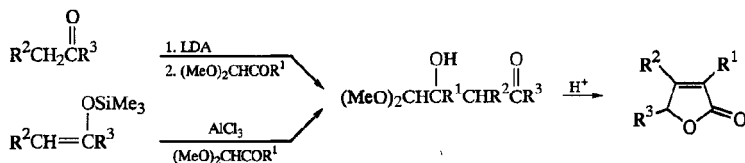
TL 28 2135 (1987); 33 4065 (1992)

JOC 59 3202 (1994)

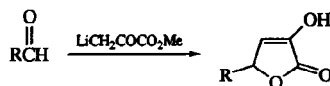




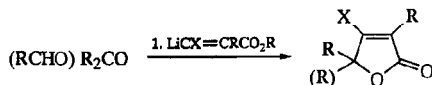
TL 36 2839 (1995)



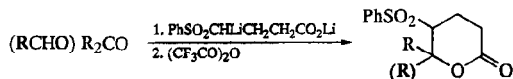
JOC 53 1560 (1988)



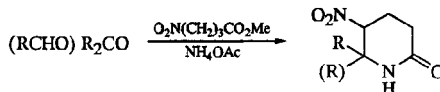
TL 29 3923 (1988)

X = OR, SR, NR₂

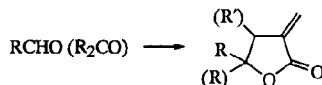
See page 351, Section 1.



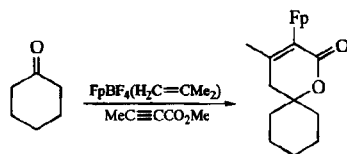
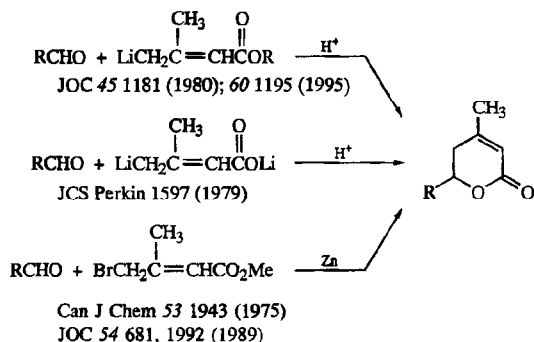
TL 28 4243 (1987)



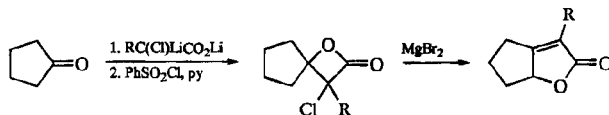
TL 34 5831 (1993)

H₂C=CBrSiMe₃, TiCl₄/CO, cat Ni(CO)₂(PPh₃)₂ JACS 104 6879 (1982)*n*-Bu₃SnCH₂C(=CH₂)CONHR, BF₃·OEt₂ or TiCl₄/H⁺ JOC 51 1856 (1986)H₂C=C(CH₂SnCl₂Br)CO₂Et TL 34 7749 (1993)H₂C=C(CH₂Br)CO₂H, Et₃N/Zn/H⁺ TL 26 5693 (1985)

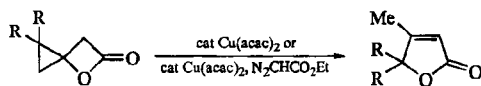
- $\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{Br})\text{CO}_2\text{H}$, In / H^+ JOC 60 4228 (1995)
 $\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{Br})\text{CO}_2\text{Me}$, In TL 32 7017 (1991)
 $\text{R}'\text{CH}=\text{C}(\text{CH}_2\text{Br})\text{CO}_2\text{Et}$, Sn(Al) / H^+ CL 541 (1986)
 $\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{Br})\text{CO}_2\text{R}$, Zn / H^+ Angew 9 457 (1970)
 J Med Chem 17 672 (1974); 18 812 (1975); 19 309 (1976); 23 1031 (1980); 25 650 (1985)
 J Pharm Sci 70 84 (1981)
 TL 26 5697 (1985)
 JOC 54 290 (1989)
 $\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{Br})\text{CO}_2\text{SiMe}_3$, Zn graphite JOC 48 4108 (1983)
 $\text{H}_2\text{C}=\text{C}(\text{CH}_2\text{OH})\text{CO}_2\text{Et}$, SnCl₂, cat PdCl₂(PhCN)₂ TL 32 225 (1991)



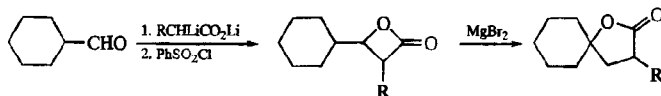
$\text{Fp} = \text{CpFe}(\text{CO})_2$
 Organomet 1 397 (1982)



TL 32 6501 (1991)



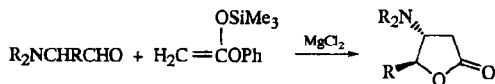
TL 35 6737 (1994)



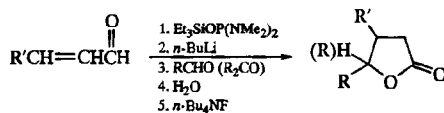
TL 28 4787 (1987)

JOC 53 2371, 5922 (1988)

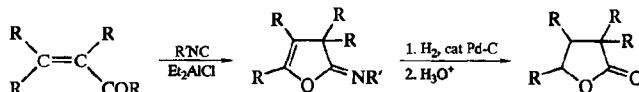
See also page 1859, Section 19.



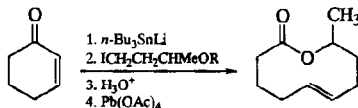
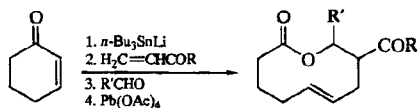
TL 30 5421 (1989)



JACS 101 371 (1979)



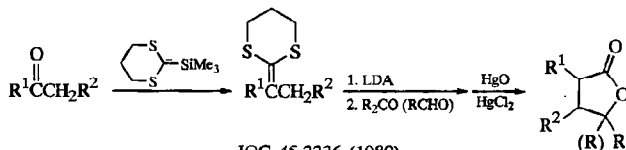
JOC 47 741 (1982)



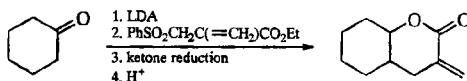
TL 28 5071 (1987)

JACS 110 4754 (1988)

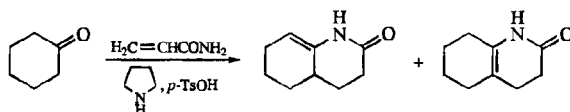
Org Syn Coll Vol 8 562 (1993)



JOC 45 2236 (1980)



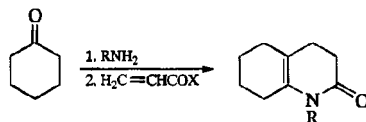
JOC 55 5977 (1990)



Pure Appl Chem 17 383 (1968) (on enamine)

CC 457 (1971) (ketone, enamine or imine)

JACS 111 4116 (1989) (ketone)



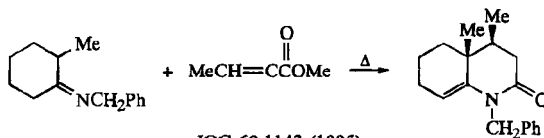
$\text{X} = \text{Cl}, \text{O}_2\text{CCH}=\text{CH}_2, \text{OH} [\text{ClCO}_2\text{Et}, (\text{PhO})_2\text{PON}_3, \text{or methyl-2-chloropyridinium iodide}]$

JCS C 1358 (1971)

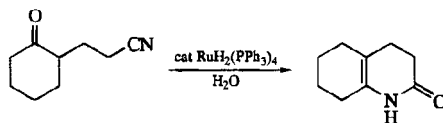
JOC 57 5319 (1992); 59 1613, 3575 (1994)

TL 34 215, 6673, 8197 (1993); 35 8813 (1994); 36 1657 (1995)

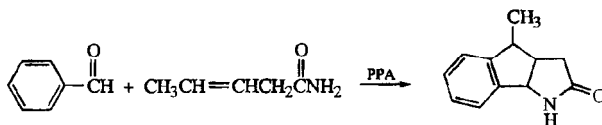
JACS 116 6201 (1994)



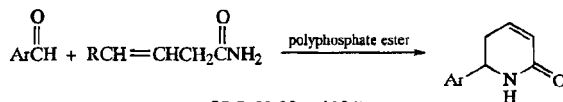
JOC 60 1143 (1995)



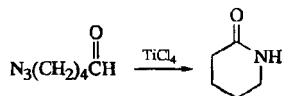
JOC 57 2521 (1992)



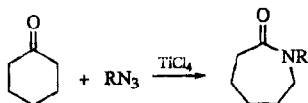
JOC 56 2603 (1991); 59 284 (1994)



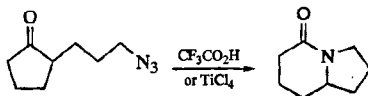
JOC 59 291 (1994)



TL 36 7811 (1995)

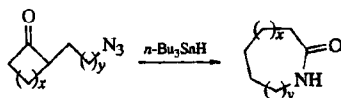


JOC 57 1635 (1992)

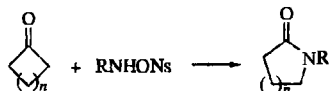


JACS 113 8965 (1991)

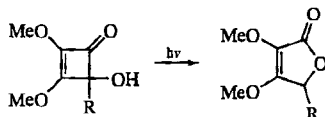
JOC 58 2933 (1993)

 $x = 1-4, y = 1, 2$

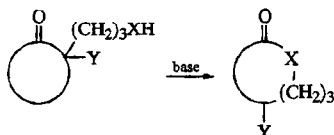
JACS 115 3328 (1993)

 $n = 1-3$

TL 30 4207 (1989)



TL 29 3529 (1988)

X

O

NH

YNO₂

CN

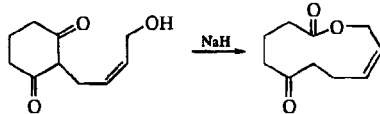
NO₂

TL 23 3521 (1982); 34 6107 (1993)

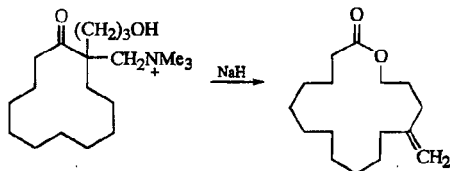
Helv 67 1713 (1984)

Helv 68 2115 (1985); 70 760 (1987)

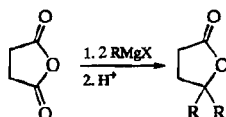
Helv 68 484 (1985)



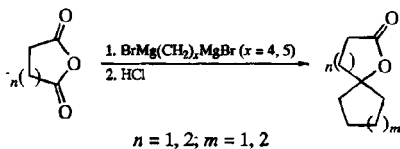
Syn 110 (1976)
JOC 52 5296 (1987)



TL 28 315 (1987)



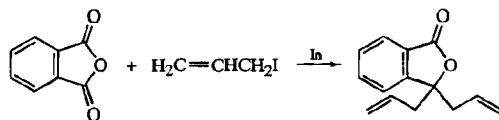
TL 22 2611 (1981)



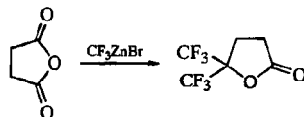
CC 125 (1980)

TL 21 4167 (1980); 22 2611 (1981); 28 4997 (1987); 32 5861 (1991)

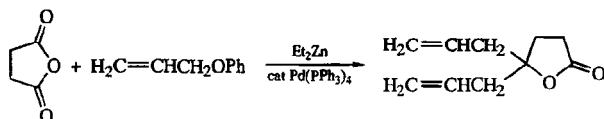
JOC 46 3091 (1981); 47 3953 (1982)



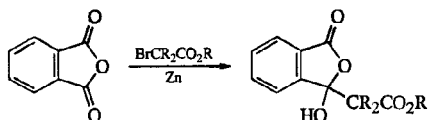
TL 30 1581 (1989)



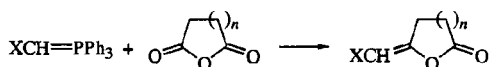
TL 29 1029 (1989)



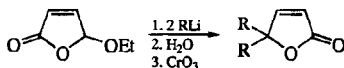
TL 34 7619 (1993)



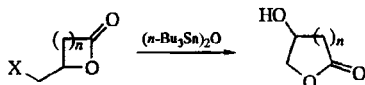
JOC 56 2587 (1991)

X = COR, CO₂R; n = 1, 2

TL 2357 (1965); 4171 (1969); 4279 (1975); 4543 (1977); 26 1667 (1985)
 Austral J Chem 27 1477 (1974); 28 2499 (1975); 33 333 (1980); 35 1903, 2077, 2277 (1982)
 JCS Perkin I 62, 89 (1979); 1448 (1981); 1855 (1982)
 Syn 197 (1981)
 Chem Pharm Bull 32 1709 (1984)
 BCSJ 60 689 (1987)
 JOC 55 6363 (1990)

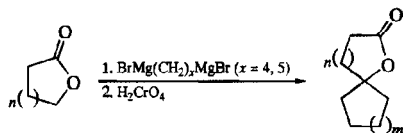


Tetr 38 2897 (1982)



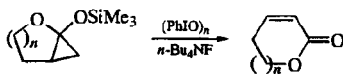
X = Br, I; n = 1, 2

JOC 56 475 (1991)



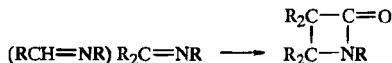
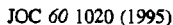
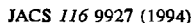
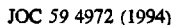
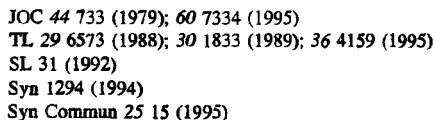
n = 0-3; m = 1, 2

JOC 45 1828 (1980)




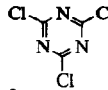
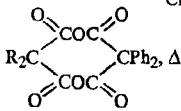
n = 1-3, 9

TL 31 197 (1990)

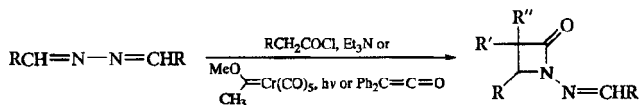


Reviews:

- Org Rxs 9 388 (1957)
Syn 327 (1973)
Chem Soc Rev 5 181 (1976)
Tetr 34 1731 (1978)
"Chemistry and Biology of β -Lactam Antibiotics," Academic Press, New York (1982), Vol 2, p 114
Heterocycles 29 2225 (1989)
Chem Rev 89 1447 (1989)

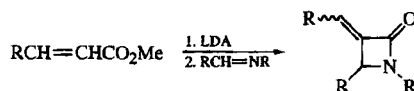
- $R_2C=C=O$
 Ann 356 51 (1907); 401 292 (1913); 760 (1977)
 Ber 50 1035 (1917); 90 2460 (1957)
 JACS 73 3172 (1951)
 Tetr 24 1011 (1968)
 CC 302 (1977)
 Syn 989 (1982)
- R_2CHCO_2H , TsCl, Et_3N
 JOC 54 2838 (1989); 58 6118 (1991)
- R_2CHCO_2H , CBr_4 , PPh_3
 Syn 689 (1976)
- R_2CHCO_2H ,  I^- , $n-Pr_3P$
 TL 32 581 (1991)
- R_2CHCO_2H , $ClPO(OR)_2$, Et_3N
 Syn Commun 6 435 (1976)
 Heterocycles 12 405 (1979)
- R_2CHCO_2H , $Cl_2PO(OR)$, Et_3N
 TL 27 4359 (1986); 29 3129 (1988); 32 5187 (1991)
 CC 1743 (1987)
 JOC 53 3784 (1988)
- R_2CHCO_2H , Cl_2PONMe_2 , Et_3N
 TL 28 1945 (1987)
- R_2CHCO_2K , $ClCO_2Et$, Et_3N
 TL 30 5239 (1989)
- RCH_2CO_2K , , Et_3N
 JOC 54 5758 (1989)
- R_2C 
 Helv 6 291, 304 (1923)
- $R_2CHCOCl$, R_3N
 JACS 73 1204, 4367 (1951); 109 1798 (1987); 113 5784 (1991); 114 9360 (1992)
 Tetr 23 4769 (1967); 36 3427 (1980)
 BSCF 2450 (1968)
 JOC 34 2846 (1969); 38 3437 (1973); 39 115, 312, 2877 (1974); 41 1112 (1976); 53 4227 (1988); 54 3792 (1989); 55 2196 (1990); 56 2244, 4418, 5385, 5948, 6968 (microwave irradiation) (1991); 57 1571, 5921 (1992); 58 307, 2454, 5771 (1993); 59 240, 932, 5184, 5856, 5858 (1994)
 TL 3167 (1971); 2633, 3135 (1974); 29 1649, 2409, 2779, 5065 (1988); 30 2321, 4577, 6619 (1989); 31 451, 1921, 3031, 3627, 6429, 6707, 7277 (1990); 32 803, 3105, 3109, 3151, 5461 (1991); 33 2111, 3603, 4819, 4823 (1992); 34 6049, 6325 (1993); 35 381, 2721, 2725, 7825 (1994); 35 213 (microwave irradiation), 497 (1994); 36 2555, 4543, 8821 (1995)
 Heterocycles 12 405 (1979)
 Syn 933 (1980); 989 (1982)
 CC 248 (1990)
 SL 749, 761 (1992); 1067 (1995)

$\text{RCOC}(\text{N}_2)\text{R}$, $h\nu$	Ber 89 2759 (1956) Tetr 23 957 (1967) BSCF 2450 (1968)
RCOCHN_2 , Ag_2O	Ber 90 2460 (1957)
$\text{RCH}_2\text{CO}_2\text{R}$, base	See page 1724, Section 2.
$\text{RCH}=\text{C}(\text{OR})\text{SiR}_3$	See page 1724, Section 2.
RCH_2COSR / LDA / SnCl_2 / imine / $\text{Hg}(\text{O}_2\text{CCF}_3)_2$	CL 293 (1987)
RCH_2COSR / LDA / Et_2AlCl / imine	TL 28 3257 (1987)
RCH_2COSR , BOTf , $i\text{-Pr}_2\text{NEt}$ / imine / $\text{KOH}/(\text{pyS})_2$, Ph_3P	TL 26 1523 (1985); 27 2149, 2153 (1986); 29 1409 (1988)
$\text{R}_2\text{CHCOS}-\text{C}_6\text{H}_4\text{N}=\text{C}_6\text{H}_4-\text{B}(\text{Cl}_3)_2\text{SMe}_2$, chiral amino alcohol / base / imine (chiral)	TL 36 613 (1995)
$\text{RCH}_2\text{COS}-\text{C}_6\text{H}_4\text{N}=\text{C}_6\text{H}_4-\text{Et}_3\text{N}$, TiCl_4	Tetr 47 8767 (1991) TL 33 1113 (1992); 34 6921 (1993) JOC 57 4155 (1992); 58 4746 (1993)
$\text{XCF}_2\text{CO}_2\text{R}$ ($\text{X} = \text{Br}, \text{I}$), Zn	TL 29 5291 (1988)
$\text{BrCHRCO}_2\text{R}$, Zn , (Me_3SiCl)	JOC 54 5736 (1989); 56 4418 (1991)
$\text{BrCR}_2\text{CO}_2\text{R}$, Zn , HgCl_2	JOC 59 5856 (1994)
$\text{RC}\equiv\text{COEt}$, Δ	Rec Trav Chim 78 551 (1959) BSCF 2450 (1968)
$\text{CH}_2=\text{C}(\text{O})-\text{CH}=\text{CH}_2$ ($\text{CH}_3\text{COCH}=\text{C}=\text{O}$ equivalent)	TL 27 6241 (1986)
$(\text{CO})_5\text{Cr}=\text{C}(\text{OR})\text{R}$, $h\nu$ (α -alkoxy β -lactam)	JACS 104 5538 (1982); 106 2680 (1994); 114 5010 (1992); 115 87 (1993); 117 3368 (1995) Tetr 41 5833 (1985) JOC 57 447, 1461 (1992); 59 4967, 7779 (1994) Org Syn Coll Vol 8 216 (1993)
$(\text{CO})_5\text{Cr}=\text{C}(\text{NR}_2)\text{R}$, $h\nu$ (α -amino β -lactam)	JACS 109 1101 (1987); 112 1109 (1990); 113 5784 (1991) JOC 53 3113 (1988); 57 447, 5453 (1992); 58 5918 (1993); 59 7934 (1994) Pure Appl Chem 62 691 (1990) (review) SL 57 (1992)
$(\text{CO})_5\text{Mo}=\text{C}(\text{OMe})\text{Me}$ (α -methoxy β -lactam)	Tetr 41 5833 (1985)

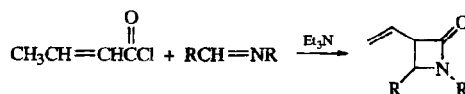


$\text{R}', \text{R}'' = \text{R}, \text{H}, \text{Me}, \text{OMe}, \text{Ph}, \text{Ph}$

JOC 54 8003 (1994)



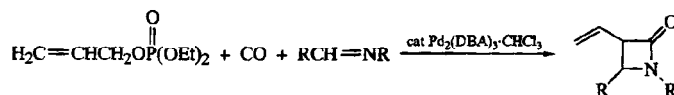
TL 31 2493 (1990)



TL 3167 (1971)

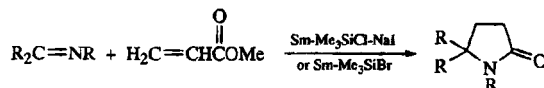
Can J Chem 57 1945 (1979)

JOC 55 575 (1990)

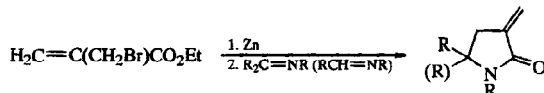


TL 34 6553 (1993)

JOC 59 3040 (1994)



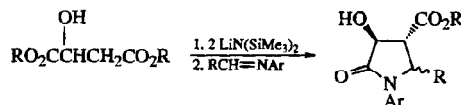
JOC 59 7902 (1994)



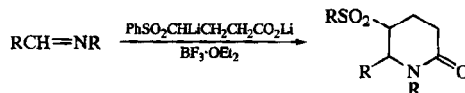
Syn Commun 15 1233 (1985)

TL 28 59 (1987)

Tetr Asym 3 511 (1992) (chiral)

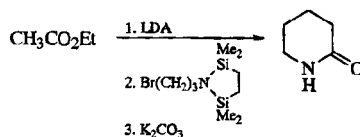


TL 36 8445 (1995)

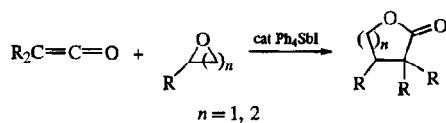


JOC 53 5389 (1988)

TL 32 5051 (1991)



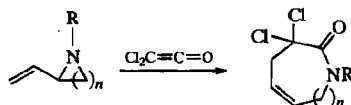
JOC 60 3916 (1995)



JOC 53 5974 (1988)



Syn 562 (1989)

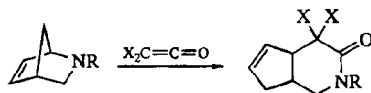
n

1

Syn 562 (1989)

3, 4

JACS 113 6690 (1991)

X

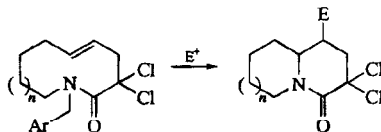
Cl

TL 32 7233 (1991)

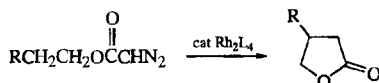
Helv 76 1591 (1993)

Ph

JCS Perkin I 1493 (1990)

 $\text{E}^+ = \text{I}_2, \text{PhSeBr}, \text{Me}_3\text{SiI} \text{ (E = H)}; n = 0, 1$

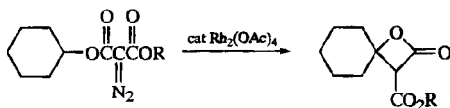
JACS 113 6690 (1991)



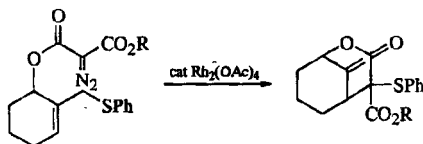
TL 30 7001 (1989); 35 3853 (1994) (chiral); 36 4745, 7579 (1995) (both chiral)
 JACS 113 8982 (1991); 115 9968 (1993); 116 4507 (1994) (all chiral)
 JOC 57 6103 (1992) (chiral, polymer); 60 3035, 6654 (chiral) (1995)



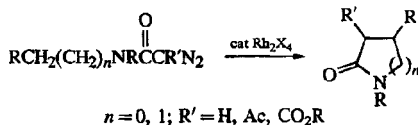
TL 30 7001 (1989); 31 1023 (1990)
JACS 115 958 (1993); 116 11323 (1994)



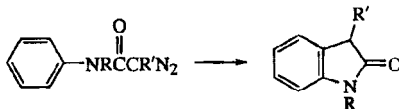
TL 36 4673 (1995)



TL 32 6159 (1991)



JOC 53 3384 (1988)
TL 30 5397 (1989); 33 7819 (1992)
JACS 115 8669, 9968 (1993)
SL 1031 (1994) (chiral); 1075 (1995) (chiral)



R

Reagent

H

Nafion-H

JOC 53 1017 (1988)

H, Ac

cat Rh₂(OAc)₄

JOC 53 1017 (1988)

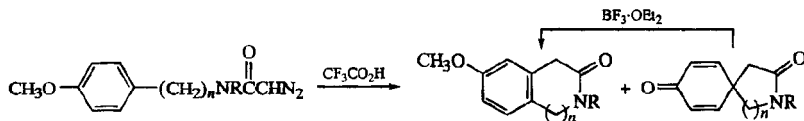
R

cat Rh₂(OAc)₄

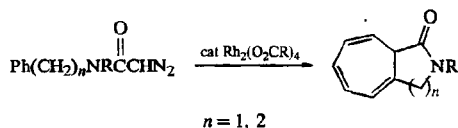
JOC 57 4404 (1992) (R' = COR, SO₂R)

cat Rh₂(NHCOCF₃)₄

JOC 59 2447 (1994) (R' = CO₂R)



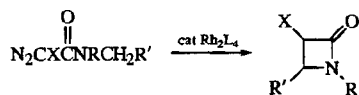
TL 29 2643 (1988)



IOC 53 3384 (1988)

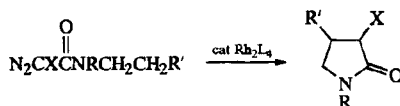
TL 29 2639 (1988)

JACS 115 8669 (1993)



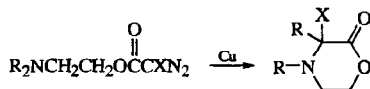
$\text{X} = \text{COR}, \text{CO}_2\text{R}$

IOC 56 820 (1991); 57 4404 (1992); 59 2447 (1994)



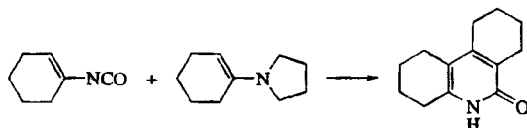
$\text{X} = \text{COR}, \text{CO}_2\text{R}, \text{SO}_2\text{R}$

IOC 56 820 (1991); 57 4404 (1992); 59 2447 (1994)

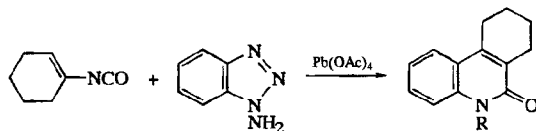


$\text{X} = \text{H}, \text{COCH}_3$

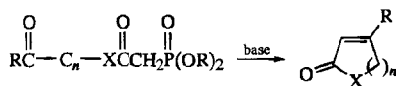
IOC 59 6051 (1994)



IOC 49 4569 (1984); 54 224 (1989)



IOC 54 4019 (1989)



X

O

Angew Int 7 300 (1968)

JACS 100 7069 (1978); 104 2030 (1982); 106 260, 1148 (1984); 108 1035 (1986); 113 8045 (1991); 117 10252 (1995)

JOC 44 4010, 4011 (1979); 55 3457 (1990)

TL 27 2157, 4873 (1986); 28 2717 (1987); 31 4703 (1990); 33 2375 (1992); 34 1039, 7899 (1993); 35 3755 (1994); 36 4741 (1995)

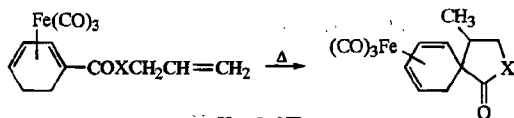
CC 413 (1986)

Tetr 43 4849 (1987)

NH

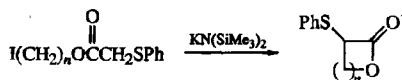
CC 445 (1970)

JACS 101 7104 (1979); 114 8008 (1992)

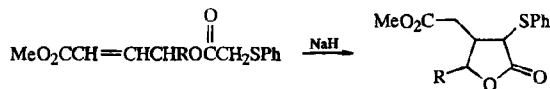


X = O, NR

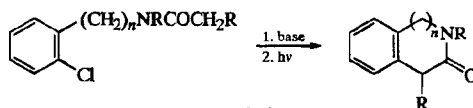
JACS 111 3908 (1989)

 $n = 7, 9, 12$

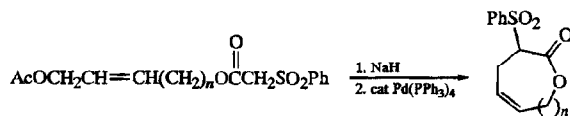
JACS 100 7424 (1978)



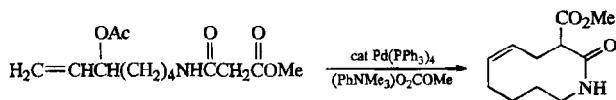
JOC 59 4461 (1994)

 $n = 0, 1$

JACS 102 3646 (1980); 107 435 (1985)

 $n = 2, 4$

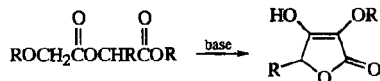
JACS 101 1595 (1979)



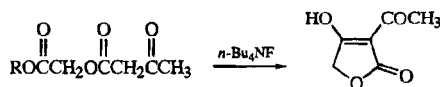
JOC 60 6595 (1995)



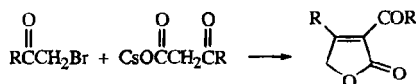
JOC 60 2016 (1995)



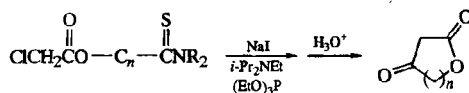
JOC 55 1112 (1990)



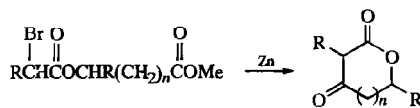
TL 29 4807 (1988)



JOC 60 286 (1995)

 $n = 1, 2, 6, 8$

JOC 45 1868 (1980)

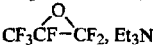
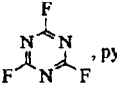
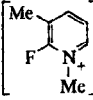
 $n = 0, 1$

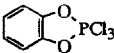
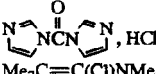
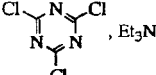
TL 34 277 (1993)

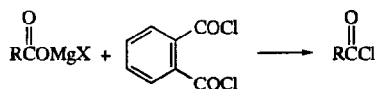
9. INTERCONVERSION OF NITRILES, CARBOXYLIC ACIDS AND DERIVATIVES

1. Carboxylic Acids to Acid Halides



<u>X</u>	<u>Reagent(s)</u>	
F	SeF ₄ , py	JACS 96 925 (1974)
	Me ₂ C=CFNMe ₂	CC 1180 (1979)
	 CF ₃ CF(NEt ₂)CF ₂ , Et ₃ N	CL 483 (1977)
	FCICHCF ₂ NEt ₂	J Gen Chem USSR 29 2125 (1959)
	[(Me ₂ N) ₂ CF]PF ₆ , <i>i</i> -Pr ₂ NEt	JACS 117 5401 (1995)
	 , py	Syn 487 (1973) JOC 57 6371 (1992); 58 6609 (1993)
Cl	 OTs ⁻ , Et ₃ N	CL 303 (1976)
	SOCl ₂	Org Syn Coll Vol 1 12, 147 (1941); 3 169, 490, 547, 555, 712 (1955); 4 154, 263, 339, 715, 739 (1963) JOC 50 2719 (1985)
	SOCl ₂ , DMF	Helv 42 1653 (1959)
	SOCl ₂ , py	JACS 75 2347 (1953) JCS 491 (1963) Can J Chem 46 2549 (1968)
	SOCl ₂ , py (on KO ₂ CR)	JACS 85 643 (1963)
	PCl ₃	Org Syn Coll Vol 2 156 (1943)
	PCl ₅	Org Syn Coll Vol 1 394 (1941) JACS 67 2239 (1945)


		Ber 96 1387 (1963) Z Chem 22 126 (1982) (review)
	CCl ₄ , Ph ₃ P	JACS 88 3440 (1966)
	CCl ₄ , polymer-PPh ₂	CC 622 (1975) JOC 48 3721 (1983)
	polymer-PPh ₂ Cl ₂	JACS 96 6469 (1974)
	PhCOCl	JACS 60 1325 (1938)
	ClCOCOC	JACS 42 599 (1920); 69 2568 (1947); 110 6528 (1988) JCS 3490 (1953) Can J Chem 33 1515 (1955)
	OH ⁻ / ClCOCOC	JOC 29 843 (1964); 56 1453 (1991) JACS 42 599 (1920); 70 2427 (1948); 87 3958 (1965) Helv 37 45 (1954) Can J Chem 33 1515 (1955)
	Cl ₂ CHOMe	TL 3379 (1977) Syn 163 (1975)
	XCH ₂ CCl ₂ OEt (X = H, Cl)	Org Syn 61 1 (1983) Org Syn Coll Vol 7 467 (1990) Rec Trav Chim 76 969 (1957)
	 , HCl	Ann 694 78 (1966)
	Me ₂ C=C(Cl)NMe ₂	CC 1180 (1979)
	 , Et ₃ N	TL 3037 (1979) Ind J Chem B 20 852 (1981)
Br	BBr ₃ -Al ₂ O ₃	TL 33 7475 (1992)
	PBr ₃	JCS 1406 (1934)
	PBr ₅	JACS 42 599 (1920)
	Ph ₃ PBr ₂	Ann 693 132 (1966) Syn 684 (1982)
	BrCOCOCBr	JACS 42 599 (1920)
	Me ₂ C=C(Br)NMe ₂	CC 1180 (1979)
I	I ₂ , H ₂ SiI ₂	JOC 55 3922 (1990)
	Me ₂ C=C(I)NMe ₂	CC 1180 (1979)

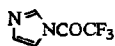
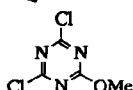


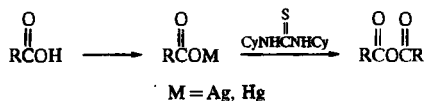
TL 30 6473 (1989)

2. Carboxylic Acids to Acid Anhydrides

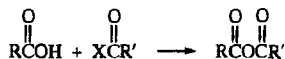


Ac ₂ O	JACS 63 699 (1941); 72 3294 (1950) Org Syn Coll Vol 1 91, 410 (1941); 3 449 (1955); 4 630, 790 (1963) JOC 53 4724 (1988); 58 142 (1993); 60 560 (1995) TL 29 5139 (1988) SL 105 (1994)
Ac ₂ O, AcCl	JOC 53 1040 (1988)
(CF ₃ CO) ₂ O	JOC 60 588 (1995)
H ₂ C=C=O	Org Syn Coll Vol 3 164 (1955)
H ₂ C=C(OAc)CH ₃ , cat H ₂ SO ₄	Ind Eng Chem 41 2920 (1949)
RCOCl, 4-vinylpyridine copolymer	TL 27 4933 (1986)
CH ₃ COCl	Org Syn Coll Vol 2 560 (1943) JACS 110 6172 (1988) JOC 53 1527 (1988) SL 40 (1993)
<i>t</i> -BuCOCl	SL 431 (1995)
COCl ₂ , Et ₃ N	Helv 47 162 (1964) Org Syn Coll Vol 5 822 (1973)
ClCOCOCl	JACS 42 599 (1920)
NaOH/ClCOCOCl	JACS 42 599 (1920); 76 5803 (1954)
ClCO ₂ Et, Et ₃ N/(Et ₃ NH)O ₂ CR	JOC 28 1905 (1963)
Cl ₃ COCO ₂ CCl ₃ , Et ₃ N	JOC 59 2913 (1994)
TsCl, py	JACS 77 6214 (1955)
SOCl ₂ , py	JACS 70 2964 (1948) JCS 741 (1952); 2117 (1953)
SOCl ₂ , 4-vinylpyridine copolymer	TL 27 4937 (1986)
ClSO ₂ NCO, Et ₃ N	Syn 506 (1982)
Tf ₂ O, Ph ₃ PO/Et ₃ N	JOC 54 1144 (1989)
POCl ₃	Org Syn Coll Vol 2 560 (1943)
(PhO) ₂ POCl, Et ₃ N	Syn 218 (1981)
(PhO)(PhNH)POCl, R ₃ N	Syn 218 (1981)
 POCl, R ₃ N	Syn 616 (1981)
Cl ₂ , (Me ₂ N) ₃ P/Et ₃ N	BSCF 3034 (1971)
(Me ₂ N) ₃ P, CCl ₄	BSCF 3034 (1971)
(Me ₂ NCCl=NMMe ₂)Cl, Et ₃ N	BCSJ 56 3529 (1983)

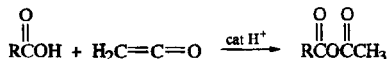
DCC	Ber 95 1076 (1962) JACS 85 1997 (1963) J Lipid Res 7 174 (1966) JOC 50 2323 (1985)
polymer-CH ₂ N=C=N- <i>i</i> -Pr	TL 3281 (1972)
PhCOCH=CHCOPh, <i>n</i> -Bu ₃ P	JOC 29 1385 (1964)
HC≡COMe	JCS 1860 (1954)
HC≡COEt	JOC 33 3808 (1968)
Me ₃ SiC≡COEt	TL 25 6027 (1984); 27 3689 (1986); 28 3971 (1987) JOC 51 4150 (1986); 56 119 (1991) CC 1474 (1987)
2,4,6-(NO ₂) ₃ C ₆ H ₂ Cl, Et ₃ N or py	BCSJ 54 1470 (1981)
	Ber 95 2073 (1962)
 , <i>N</i> -methylmorpholine	TL 26 2901 (1985)



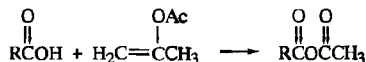
BCSJ 41 2746 (1968)



See page 1951, Section 8.



JACS 54 3427 (1932)



Ind Eng Chem 41 2920 (1949)

3. Carboxylic Acids to Esters

See also page 1861, Section 8.


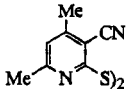
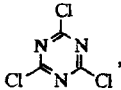
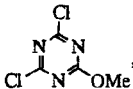
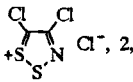



Reviews:

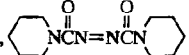


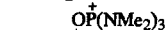
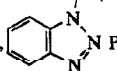



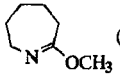
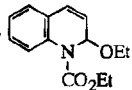
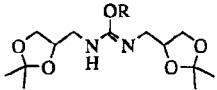
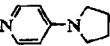
Tetr 36 2409 (1980)

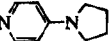


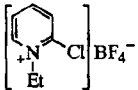
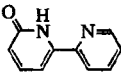



"Preparative Biotransformations," Ed. S. M. Roberts, J. Wiley, New York (1992) (enzymes)


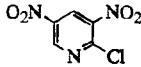
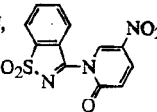
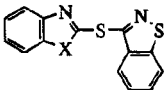
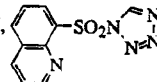
- alkene, H_2SO_4 Org Syn Coll Vol 4 261, 417 (1963)
JOC 54 3907 (1989)
- ROH, microwave irradiation JOC 57 6231 (1992)
- ROH, lipase (enantioselective) Proc Natl Acad Sci USA 82 3192 (1985)
JACS 107 7072 (1985); 109 2812 (1987); 113 2253 (1991)
TL 26 1857 (1985); 27 29 (1986); 28 1647 (1987);
29 5133 (1988); 34 801, 5791 (1993)
JOC 52 3477 (1987); 58 3238, 4656 (1993); 59 4410 (1994); 60 2244 (1995)
- ROH, immobilized lipase TL 33 5891 (1992)
- ROH, Dowex 50H^+ TL 34 1181 (1993)
- ROH, HCl Org Syn Coll Vol 1 237, 451 (1941); 2 261, 276, 292 (1943)
JOC 52 4689 (1987); 60 8318 (1995)
- ROH, H_2SO_4 Org Syn Coll Vol 1 241, 254 (1941); 2 264, 365, 414 (1943); 3 381 (1955); 4 329, 532, 635 (1963); 5 762 (1973); 8 258 (1993)
JOC 50 2128 (1985)
- 100% H_2SO_4 / ROH JACS 63 2431 (1941)
- ROH, H_2SO_4 , HC(OR)_3 TL 29 1421 (1988)
- ROH, supported H_2SO_4 S Afr J Chem 36 81 (1983)
- ROH, MeSO_3H Org Syn Coll Vol 7 319 (1990)
- ROH, TsOH Org Syn Coll Vol 3 610 (1955)
- ROH, graphite bisulfate JACS 96 8113 (1974)
- ArOH, B(OH)_3 , H_2SO_4 TL 3455 (1971)
- ROH, $\text{BF}_3 \cdot \text{OEt}_2$ TL 4011 (1970)
Syn 316 (1971); 628 (1972)
JACS 108 468 (1986)
JOC 57 441 (1992)
- ROH, $\text{BF}_3 \cdot 2\text{MeOH}$ ($\text{R}' = \text{H}$) Org Prep Proc Int 14 177 (1982)
- ROH, AlCl_3 -polymer TL 1823 (1973)
- ROH, cat $\text{R}'_2\text{SnCl}_2$ ($\text{R}' = \text{Me}, \text{Ph}$) TL 28 3713 (1987)
- ROH, cat $\text{SCNSn}(n\text{-Bu})_2\text{OSn}(n\text{-Bu})_2\text{OH}$ JOC 56 5307 (1991)
- $\text{Sn} \left(\text{C}_5\text{H}_4\text{Me} \right)_2 / \text{ROH}$ CL 683 (1983)

$R_3N/$  , Ph_3P/ROH	CL 979 (1978)
 , PPh_3/ROH	Angew Int 18 308 (1979)
 , Et_3N/ROH	TL 3029, 3037 (1979) Ind J Chem B 20 852 (1981)
 , <i>N</i> -methylmorpholine/ ROH	TL 26 2901 (1985)
 Cl^- , 2,6-lutidine/ ROH	TL 34 2737 (1993)
$ClSO_2NCO$, Et_3N/ROH	Syn 506 (1982)
SO_2ClF , Et_3N/ROH , Et_3N	Syn 790 (1981)
$SOCl_2$, DMAP/ ROH , DMAP	Syn Commun 12 1139 (1982)
$MsCl$, Et_3N/ROH	TL 23 3799 (1982) Syn Commun 12 727 (1982)
$TsCl$, py/ROH	JACS 77 6214 (1955)
Tf_2O , $Ph_3PO/ROH/Et_3N$	JOC 54 1144 (1989)
ROH , Me_3SiCl	BCSJ 54 1267 (1981) Syn 201 (1983) Ind J Chem B 22 505 (1983)
$MeOH$, CH_3COCl ($R = Me$)	JACS 108 1039 (1986)
2,4,6- $Cl_3C_6H_2COCl$, NEt_3/ROH , DMAP	BCSJ 52 1989 (1979) JACS 108 4645 (1986); 115 9925 (1993) TL 31 1735 (1990); 36 7101 (1995) JOC 58 2862 (1993); 60 5048 (1995)
α - $BrCH_2C_6H_4COBr$, Et_3N/ROH	CL 145 (1979)
α - $BrCH_2C_6H_4COBr$, $Et_3N/AgBF_4$, ROH	TL 28 4711 (1987)
t - BuO_2CF , Et_3N , cat DMAP, t - $BuOH$, CH_2Cl_2 ($R = t$ - Bu)	TL 30 6859 (1989)
RO_2CCl , py/ROH	TL 28 1665 (1987)
RO_2CCl , Et_3N /cat DMAP	TL 24 3365 (1983) JOC 50 560 (1985)
ROH , $H_2C=C(CH_3)OCOCl$, <i>N</i> -methylmorpholine	JACS 112 7659 (1990)
ROH , $H_2C=C(CH_3)OCOCl$, Et_3N or py , (cat DMAP)	TL 28 1661, 1665 (1987)


- (COCl)₂, DMF/ROH, py *Helv* 61 1675 (1978)
- ROH, Ac₂O, cat DMAP, Et₃N (R' = H) *Angew Int* 17 569 (1978)
- (CF₃CO)₂O/ROH *Chem Rev* 55 787 (1955)
 TL 1285 (1964)
Tetr 21 3531 (1965)
JOC 30 927 (1965)
Can J Chem 59 2617 (1981)
- (CF₃CO)₂O, NaF/ROH *Can J Chem* 59 2617 (1981)
- ROH, (p-NO₂C₆H₄CO)₂O, cat Sc(OTf)₃ *JACS* 117 4413 (1995)
- H₂C=C(Me)OCO₂CO₂CH₂CH=CH₂, cat DMAP
 (R = CH₂CH=CH₂) *TL* 36 113 (1995)
- ROH, PPh₃, CCl₄ (on KO₂CR') *JOC* 50 4991 (1985)
- ArOH, PPh₃, CCl₄, Et₃N (R = Ar) *BCSJ* 54 2227 (1981)
- NBS or NIS, PPh₃, molecular sieves/ROH, py *TL* 35 4415 (1994)
- ROH (R = 2°, 3° alkyl), n-Bu₃P·I₂, HMPA *Austral J Chem* 35 517 (1982)
- Ph₃P(OTf)₂/ROH *TL* 277 (1975)
- py/Me₂NPOCl₂ or PhOPOCl₂/ROH *TL* 4461 (1978)
- PhOPOCl₂, DMF/ROH/py *Syn Commun* 12 681 (1982)
- PhOPOCl₂, DMF/ROH/Et₃N *JACS* 113 1409 (1991)
- n-BuLi/(EtO)₂POCl/ROH *JOC* 52 3937 (1987)
- ₂POCl, Et₃N/ROH *Syn* 547 (1980)
- Cl₃CPO(OEt)₂ (R = Et) *Tetr* 38 1457 (1982)
- ROP(OEt)₂, EtO₂CN=NCO₂Et (R = Et, allyl) *BCSJ* 40 2380 (1967)
- ROP(NEt₂)₂, EtO₂CN=NCO₂Et *BCSJ* 44 3427 (1971)
- ROH, R''O₂CN=NCO₂R'', Ph₃P *BCSJ* 40 2380 (1967); 44 3427 (1971)
TL 1619 (1973); 27 5813 (1986) (on pyranose hemiacetals); 30 325 (sugars), 6645 (1989); 31 2201, 5253 (1990); 32 3017 (1991); 33 4317 (1992); 34 1195, 6833 (1993); 35 5081, 8341 (1994)
Syn 1 (1981) (review)
JOC 52 3468, 3784 (1987); 54 3045, 3049 (1989); 56 2883 (1991); 59 234 (1994)
JACS 109 3017 (1987); 110 6487 (1988) (mechanism); 111 3974 (1989) (polymer-supported azodicarboxylate); 113 2092, 2112 (1991)
Org Rxs 42 335 (1992) (review)
- ROH, EtO₂CN=NCO₂Et, PPh₃/NaO₂CPh *JOC* 52 4235 (1987)

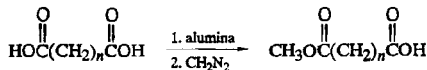
- ROH, $\text{EtO}_2\text{CN}=\text{NCO}_2\text{Et}$, polymer- PPh_2 JOC 48 3598 (1983)
- ROH, , $n\text{-Bu}_3\text{P}$ TL 34 1639 (1993)
- ROH, $\text{Me}_2\text{NCON}=\text{NCONMe}_2$, $n\text{-Bu}_3\text{P}$ TL 35 5081 (1994); 36 2529 (1995)
- ROH, $n\text{-Bu}_3\text{P}=\text{CHCN}$ TL 35 5081 (1994)
- ROH, $(\text{PhO})_2\text{PO}_2$ , Et_3N JOC 50 760 (1985)
- $(\text{EtO})_2\text{PON}$ , $\text{Et}_3\text{N}/\text{ROH}$ CL 123 (1985)
- ROH, , $\text{OP}^+(\text{NMe}_2)_3$ TL 35 5603 (1994)
- ROH, , PF_6^- , $i\text{-Pr}_2\text{NEt}$ JOC 49 4877 (1984)
- $[(\text{RO})_3\text{PCH}_3]\text{BF}_4$ (on $\text{R}'\text{CO}_2\text{H}$ or $\text{R}'\text{CO}_2\text{Na}$) Chem Ind 2102 (1964)
- $\text{P}_2\text{O}_5/\text{ArOH}$ ($\text{R}=\text{Ar}$) Syn 429 (1979)
- ArOH, polyphosphate ester, DMF ($\text{R}=\text{Ar}$) CC 473 (1985)
- ROH, , O_2CO , cat DMAP Angew Int 1 351 (1962)
- , ROH, Δ or NaOR JACS 111 4856 (1989)
- , $t\text{-BuOH}$, DBU ($\text{R}=t\text{-Bu}$) TL 29 2483 (1988)
- $\left[\text{CH}_3\text{-N}^+\text{CON}^+\text{CH}_3\right]$ $(\text{OTf})_2/\text{ROH}$ JACS 117 12721 (1995)
-  ($\text{R}=\text{Me}$) JOC 60 7072 (1995)
- $\text{Cl}_3\text{CC}(\text{=NH})\text{O}-i\text{-Bu}$, $\text{BF}_3\cdot\text{OEt}_2$ ($\text{R}=i\text{-Bu}$) Ber 100 16 (1967)
- ROH,  CO_2Et Syn 561 (1979) (review)
- $\text{R}'\text{NHC}(\text{OR})=\text{NR}'$ ($\text{R}'=i\text{-Pr}$, $c\text{-C}_6\text{H}_{11}$) TL 34 975, 6863 (1993)
-  JOC 59 7503 (1994)
- ROH, $i\text{-PrN}=\text{C}=\text{N}-i\text{-Pr}$,  JACS 113 8045 (1991)

ROH, DCC	Tetr 21 3531 (1965) Ber 100 16 (1967) Tetr 37 233 (1981) (review) Chem Rev 81 589 (1981) (review)
ArOH, DCC	Compt Rend 256 1804 (1963) Tetr 21 3531 (1965) JOC 58 100 (1993)
ROH, DCC, TsOH	Acta Chem Scand B 33 410 (1979)
ROH, DCC, (cat) DMAP	Angew Int 17 522 (1978) Syn Commun 9 539 (1979) CC 1132 (1982) Org Syn 63 183 (1984) JACS 108 3112 (1986) TL 28 4019 (1987); 30 3569, 3585, 4525 (1989); 31 5253 (1990); 35 105, 1651 (1994) Org Syn Coll Vol 7 93 (1990) JOC 59 2577, 4805 (1994)
DCC, DMAP, DMAP·HCl/ROH	JOC 50 2394 (1985)
ROH, DCC, cat 	TL 4475 (1978); 4483 (1994)
ROH, DCC, cat  -NMe-polymer	BCSJ 54 631 (1981)
ROH, (EtN=C=C(CH ₂) ₃ NMe ₂)·HCl, DMAP	JOC 47 1962 (1982) JACS 112 5230 (1990) TL 35 197 (1994)
ROH, [Me ₂ NCCl= ⁺ NMe ₂]Cl ⁻ , py	CL 1891 (1982)
ROH,  BF ₄ ⁻ , CsF	CL 391 (1980)
 BF ₄ ⁻ ,  /ROH, CsF	CL 563 (1980)
ROH,  OTs ⁻ , Et ₃ N	JOC 57 4027 (1992)
ROH,  I ⁻ , Et ₃ N	TL 29 2139 (1988); 30 3209 (1989) JOC 57 4664 (1992)
ROH,  I ⁻ , n-Bu ₃ N (X = Cl, Br)	CL 1045 (1975)

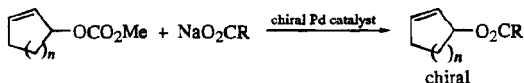
ROH,  Y^- , $n\text{-Bu}_3N$ ($R' = \text{Me, Et}$) $X = \text{Cl, Br}; Y = \text{I, BF}_4$	BCSJ 50 1863 (1977)
ROH,  , py ($R' = \text{aryl}$)	BCSJ 56 639 (1983)
2,4,6-(NO ₂) ₃ C ₆ H ₂ F, Et ₃ N/ROH	BCSJ 51 1866 (1978)
2,4,6-(NO ₂) ₃ C ₆ H ₂ F, DMAP, ROH	Syn Commun 11 121 (1981)
ROH, 2,4,6-(NO ₂) ₃ C ₆ H ₂ Cl, DMAP	Syn Commun 11 121 (1981)
ROH, 2,4,6-(NO ₂) ₃ C ₆ H ₂ Cl, py	BCSJ 54 1470 (1981)
ROH, Et ₃ N, 	CL 1161 (1980)
 , Et ₃ N ($X = \text{O, S}$)	Syn 933 (1982)
ROH, Et ₃ N, 	Chem Pharm Bull 30 2633 (1982)
(R ₃ O)BF ₄ ($R = \text{Me, Et}$), $i\text{-Pr}_2\text{NEt}$	TL 4741 (1971) JOC 44 1149 (1979); 59 2092 (1994) Org Syn Coll Vol 6 576 (1988)
Me ₃ SOH ($R = \text{Me}$)	JOC 44 638 (1979)
K ₂ CO ₃ /R ₃ SOX or RSPH ₂ X ($X = \text{BF}_4, \text{ClO}_4$; phase transfer)	Syn 926 (1980) Tetr 39 3111 (1983)
Me ₃ SeOH ($R = \text{Me}$)	TL 1787 (1979)
Me ₄ NOH/ Δ ($R = \text{Me}$)	JACS 61 1290 (1939)
(R ₃ NCH ₂ Ar)OH, Δ ($R = \text{CH}_2\text{Ar}$)	Syn 727 (1974) Austral J Chem 28 2065 (1975)
NaOH/ $n\text{-BuSO}_3\text{Cl}/\Delta$ ($R = n\text{-Bu}$)	JACS 69 1046 (1947)
NaOH or K ₂ CO ₃ /Me ₂ SO ₄ ($R = \text{Me}$)	TL 757 (1972)
Me ₂ SO ₄ , alumina	BCSJ 59 2481 (1986)
Et ₂ SO ₄ , DBN ($R = \text{Et}$)	Syn Commun 6 89 (1976)
(RO) ₂ SO, cat H ₂ SO ₄ ($R = \text{Me, Et}$)	Ind J Chem B 21 259 (1982)
HC \equiv CCHR''SC(S)OR ($R = 1^\circ, 2^\circ$ alkyl)	JACS 116 9739 (1994)
R ₂ CHOMs, CsF	SL 336 (1995)

MeBr, K ₂ CO ₃ , DMF (R = Me)	Syn Commun 7 559 (1977)
MeI, NaHCO ₃ , DMF (R = Me)	JOC 59 3775 (1994)
MeI, KOH, HMPA, EtOH (R = Me)	TL 4063 (1972)
MeI, KOH, DMSO (R = Me)	Tetr 31 2169 (1979); 35 2169 (1979)
MeI, CaO, DMSO (R = Me)	Syn 262 (1972)
RX, Cs ₂ CO ₃ , DMF	JOC 46 4321 (1981); 60 8262 (1995) TL 33 1969 (1992)
RX, CsF, DMF (R = 1°, 2° alkyl)	JOC 57 2166 (1992)
(<i>n</i> -Bu ₃ Sn) ₂ O/1° RX, CsF, DMF	JOC 57 2166 (1992)
EtI, anion exchange resin (R = Et)	JOC 44 2425 (1979)
RX, anion exchange resin (R = 1°, 2° alkyl; benzyl)	Syn 723 (1975) Syn Commun 12 327 (1982)
RX, ion exchange resin (on KO ₂ CR'; R = 1° alkyl, benzyl)	JOC 54 4993 (1989)
RX, Me ₄ NCl-silica (on KO ₂ CR'; R = 1° alkyl)	JOC 55 2952 (1990)
PhCH ₂ Br, crown ether (on KO ₂ CR')	JCS Perkin II 317 (1983)
RX, NaHCO ₃ , DMF (R = 1°, 2° alkyl)	Syn 961 (1979)
RX, NaHCO ₃ , [(<i>n</i> -C ₈ H ₁₇) ₃ NCH ₃]Cl, CH ₂ Cl ₂ (R = 1° alkyl, benzyl)	Syn 957 (1979)
CsCO ₃ or Cs(HCO ₃) ₂ /RX, DMF (R = 1°, 2°, 3° alkyl; benzylic; X = halogen or sulfonate ester)	Helv 56 1476 (1973) JOC 42 1286 (1977); 46 4321 (1981); 52 3777, 4230 (1987) Syn Commun 13 553 (1983) CL 1555 (1984) TL 26 5257 (1985); 28 1873 (1987) JACS 114 6630 (1992)
1°, 2° RI; K ₂ CO ₃ or KOH; acetone	JOC 44 2425 (1979)
MeI or EtI, K ₂ CO ₃	JOC 50 2668 (1985)
<i>t</i> -BuBr, K ₂ CO ₃ , (PhCH ₂ NEt ₃)Cl	TL 34 7409 (1993)
RX, alumina (on KO ₂ CR'; RX = 1°, 2° alkyl bromide; 1° alkyl sulfonate)	Syn Commun 10 279 (1980)
K ₂ CO ₃ or NaOH/1°, 2° RX, HMPA	TL 689 (1973) JOC 39 1968 (1974)
KOH/RX, <i>n</i> -Bu ₄ NBr or Aliquat 336 (RX = 1°, 2° alkyl bromides; benzyl and allyl bromide; MeI; 1° alkyl sulfates)	Syn 40 (1985)
Me ₄ NOH/RX, DMF	Syn Commun 2 215 (1972)

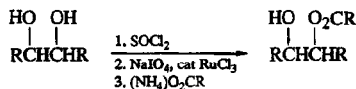
 / RX, DMF (R = 1°, 2° alkyl; benzylic; allylic)	JOC 51 546 (1986)
1° RBr, Et ₃ N	JACS 111 3640 (1989)
RBr, phosphoramidate or polyamine (on KOAc; R = 1° alkyl, allyl, benzyl, α-keto)	Syn 805 (1975)
1°, 2° RX; DBU (X = Br, I)	BCSJ 51 2401 (1978) Org Prep Proc Int 12 225 (1980) JOC 60 4412 (1995)
RX, KF (RX = 1° RCl, 1° RBr, RCHClCO ₂ H)	JACS 99 498 (1977)
ArCH ₂ Br, KF	JOC 55 1585 (1990)
Cu ₂ O; 1°, 2° RX (X = Br, I); CyN≡C	Syn Commun 2 1 (1972)
R ₂ CH ₂ CH ₂ I, base, electrolysis	JOC 53 5714 (1988)
<i>t</i> -BuOAc, HClO ₄ (R = <i>t</i> -Bu)	Ann 646 134 (1961)
(MeO) ₃ CH, MeOH, cat TsOH (R = Me)	JOC 50 2607 (1985)
(EtO) ₃ CH (R = Et)	Chem Ind 349 (1965)
(EtO) ₃ CCH ₃ (R = Et)	TL 34 7355 (1993)
(EtO) ₃ CCH ₃ , cat TsOH (R = Et)	TL 34 7355 (1993)
(RO) ₂ CHNMe ₂	Angew 75 296 (1963) (2 publications) Angew Int 2 211, 212 (1963) Helv 48 1746 (1965) Ann 821 (1974) Tetr 35 1675 (1979) Syn 135 (1983) JOC 60 6277 (1995)
CH ₂ N ₂ (R = Me)	Org Syn Coll Vol 2 165 (1943) JACS 76 4481 (1954) Ber 89 933 (1956) Org Syn 41 16 (1961) J Chem Ed 47 710 (1970) TL 1397 (1973) JOC 47 578, 1962 (1982); 50 2323, 2607 (1985); 53 3046 (1988)
Me ₃ SiCHN ₂ , MeOH (R = Me)	Chem Pharm Bull 29 1475 (1981) JOC 58 4979 (1993); 60 3859 (1995)
<i>i</i> -Pr ₃ SiCHN ₂ [R = CH ₂ Si(<i>i</i> -Pr) ₃]	TL 34 4905 (1993)
PhCHN ₂ (R = CH ₂ Ph)	JOC 60 650 (1995)
RCOCHN ₂ (R = CH ₂ COR)	TL 34 5879 (1993)



JACS 107 1365 (1985)

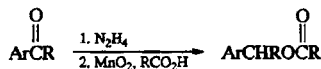
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JACS 116 10320 (1994)

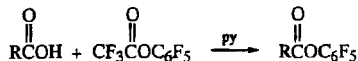


JACS 110 7538 (1988)

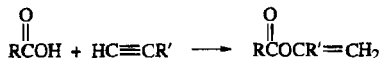
TL 30 655 (1989)



JOC 55 1585 (1990)



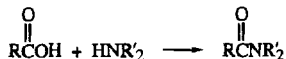
TL 31 5851 (1990)



See page 1636, Section 5.

4. Carboxylic Acids to Amides

Reviews: Syn 453 (1972); 549 (1974) (both peptide coupling)



Δ

JACS 53 1879 (1931); 59 401 (1937); 71 2215 (1949)

Org Syn Coll Vol 1 3, 83, 111 (1941); 3 590 (1955)

JOC 8 473 (1943)

Δ, molecular sieves (only 1° amine)

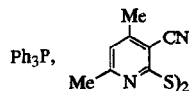
TL 30 2771 (1989)

NaBH₄

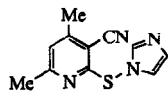
JOC 40 3453 (1975)

Syn 766 (1978)

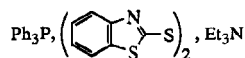
$\text{BH}_3 \cdot \text{Me}_3\text{N}$	Syn 1013 (1983)
$\text{BH}_3 \cdot n\text{-Bu}_3\text{N}$	Tetr 26 1539 (1970)
HB(OR)_2 ($\text{R} = i\text{-Pr}, t\text{-Am}$)	Tetr 26 1539 (1970)
CB	JOC 43 4393 (1978)
ClB(OMe)_2	Tetr 26 1539 (1970)
BX_3 ($\text{X} = n\text{-C}_8\text{H}_{17}, \text{OMe}$)	Tetr 26 1539 (1970)
$\text{Sn} \left(\begin{array}{c} \text{Me} \\ \\ \text{C}_5\text{H}_5 \end{array} \right)_2$	CL 683 (1983)
$\text{Sn}[\text{N}(\text{SiMe}_3)_2]$	TL 34 5193 (1993)
TiCl_4	Can J Chem 48 983 (1970)
$\text{Cp}_2\text{TiCl}_2, \text{Et}_3\text{N}$	TL 31 7281 (1990)
$\text{Cp}_2\text{ZrCl}_2, \text{Et}_3\text{N}$	TL 31 7281 (1990)
TaCl_5	TL 31 7281 (1990)
CpTaCl_4	JACS 114 6649 (1992)
TsCl, py	JACS 77 6214 (1955)
TsCl, DMAP	JOC 55 4242 (1990) JACS 113 9693 (1991)
$\text{SO}_2\text{ClF}, \text{Et}_3\text{N}$ (1° amines)	Syn 661 (1980)
$\text{ClSO}_2\text{NCO}, \text{Et}_3\text{N}$	Syn 506 (1982)
PCl_3	TL 31 1705 (1990)
P_2I_4	CL 449 (1983)
$\text{Ph}_3\text{P}, \text{Br}_2, \text{Et}_3\text{N}$	TL 25 4841 (1984)
$\text{Ph}_3\text{P}, \text{CCl}_4$ or BrCCl_3	JOC 36 1305 (1971)
polymer- $\text{PPh}_2, \text{CCl}_4$	JOC 48 3721 (1983)
$\text{R}_3\text{P}, \text{CX}_4$ ($\text{R} = n\text{-Bu}, \text{Ph}, \text{NR}_2; \text{X} = \text{Cl}, \text{Br}$)	TL 3595 (1971)
$\text{P(NMe}_2)_3, \text{COCl}_2$	Ber 116 2037 (1983)
$\text{P(NMe}_2)_3, \text{CCl}_4$	BSCF 3034 (1971)
$[(\text{Me}_2\text{N})_3\text{PBr}]\text{PF}_6, i\text{-Pr}_2\text{NEt}$	TL 31 669 (1990)
$\left[\left(\begin{array}{c} \text{N} \\ \\ \text{C}_5\text{H}_5 \end{array} \right)_3 \text{PX} \right] \text{PF}_6$ ($\text{X} = \text{Cl}, \text{Br}$), $i\text{-Pr}_2\text{NEt}$	TL 32 1967 (1991) JOC 57 5566 (1992); 59 2437 (1994)
$n\text{-Bu}_3\text{P}, o\text{-NO}_2\text{C}_6\text{H}_4\text{SCN}$	JOC 44 2945 (1979)
$\text{Ph}_3\text{P}, (\text{ArS})_2$, metal reagents	BCSJ 44 1373 (1971)
$\text{Ph}_3\text{P}, \begin{array}{c} \text{C}_6\text{H}_4 \\ \\ \text{N} \\ \\ \text{S}_2 \end{array}$	TL 1901 (1970) Ann 1254 (1985)



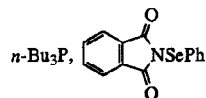
Ann 1254 (1985); 935 (1987)
Syn 236 (1987)



Ann 935 (1987)



Syn 287 (1981)



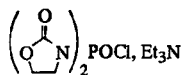
JOC 46 1215 (1981)



JOC 54 1144 (1989)



TL 277 (1975)



Syn 547 (1980); 413 (1984)
JACS 107 1421, 4342 (1985)
JOC 59 5192 (1994)



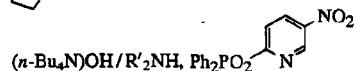
Syn 288 (1982)
TL 28 4875 (1987)



Syn 385 (1980)



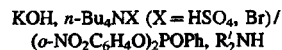
TL 25 4825 (1984)



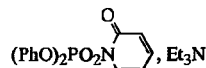
CL 1367 (1981)



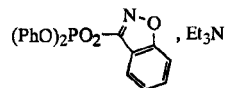
TL 32 6711 (1991); 35 2121 (1994)
JACS 117 2479 (1995)



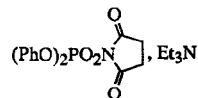
CL 285 (1981)



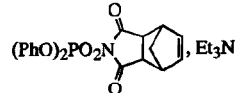
CC 719 (1986)



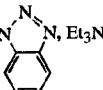
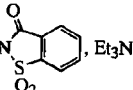

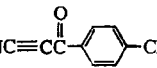

JOC 50 760 (1985)


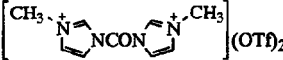

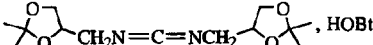


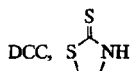
TL 21 1467 (1980)



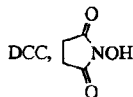
CC 1029 (1980)

$(\text{EtO})_2\text{PON}$  $\text{N}, \text{Et}_3\text{N}$	TL 26 1341 (1985)
$(\text{EtO})_2\text{PON}$  Et_3N	CL 123 (1985)
$(\text{PhO})_2\text{PON}$ 	TL 22 1257 (1981)
$(\text{PhO})_2\text{PON}_3, \text{NaHCO}_3$	JOC 52 764 (1987)
$(\text{PhO})_2\text{PON}_3, \text{Et}_3\text{N}$	JACS 94 6203 (1972)
	Chem Pharm Bull 30 3147 (1982)
	Syn 236 (1987)
	JOC 59 6190, 7671 (1994)
	SL 250 (1994)
$(\text{EtO})_2\text{POCN}, (\text{Et}_3\text{N})$	TL 1595 (1973); 32 1063 (1991); 33 5075 (1992); 36 7545 (1995)
	Chem Pharm Bull 30 3147 (1982)
	JACS 111 1524 (1989)
	JOC 57 6696 (1992); 59 3642 (1994)
propanephosphonic anhydride, R_3N	Angew Int 19 133 (1980)
$\text{Ph}_3\text{SbO}, \text{P}_4\text{S}_{10}, \text{HOAc}$	JOC 56 4076 (1991)
$\text{Me}_3\text{SiC}\equiv\text{COEt}, \text{cat HgO}$	JOC 51 4150 (1986)
$\text{R}_2\text{NC}\equiv\text{CCOR}$	Helv 61 2428, 2437 (1978)
MeN 	Org Syn Coll Vol 7 30 (1990)
$\text{CF}_3\text{CF}(\text{O})\text{CF}_2, \text{Et}_3\text{N}$	CL 483 (1977)
RO_2CCF_3 ($\text{R} = p\text{-NO}_2\text{C}_6\text{H}_5$ or C_6F_5)	Ann 1254 (1985)
$\text{MeO}_2\text{CCl}, \text{Et}_3\text{N}$ or <i>N</i> -methylmorpholine	Syn 385 (1980)
$\text{MeO}_2\text{CCl},$ 	TL 2697 (1971)
$\text{EtO}_2\text{CCl}, \text{Et}_3\text{N}$	Ann 673 186 (1964)
	JCS C 3540 (1971)
	JCS Perkin I 2909 (1982)
	JOC 58 1425 (1993)
$\text{EtO}_2\text{CCl}, \text{py}$	JOC 59 3642 (1994)
$\text{EtO}_2\text{CCl}, N\text{-methylmorpholine}$	Org Syn Coll Vol 8 132 (1993)
<i>i</i> -BuO ₂ CCl, Et_3N	Syn 385 (1980)
	JACS 113 7388 (1991); 114 7969 (1992)
	JOC 60 4177 (1995)

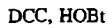
- i*-BuO₂CCl, 2,6-lutidine JACS 112 760 (1990)
- i*-BuO₂CCl, *N*-methylmorpholine Syn 385 (1980)
JOC 50 2323 (1985); 52 764 (1987); 56 5380 (1991);
58 7948 (1993)
JACS 110 7447 (1988); 111 3368 (1989)
- i*-BuO₂CCl, *N*-methylmorpholine / Et₃N TL 35 5173 (1994)
- H₂C=C(Me)O₂CCl, *N*-methylmorpholine JOC 59 5192 (1994)
- (*t*-BuOCO)₂O, py / (NH₄)HCO₃ TL 36 7115 (1995)
- t*-BuCOCl, Et₃N Tetr 11 39 (1960)
- t*-BuCOCl, DMAP, py TL 28 1131 (1987)
- 
- 
- Angew Int 1 351 (1962)
JOC 57 3454 (1992); 58 4043 (1993); 59 1418 (1994)
- JACS 111 4856 (1989)
- 1-cyclohexyl-3-(2-morpholinoethyl)carbodiimide metho-4-*p*-toluenesulfonate TL 28 3163 (1987)
- EtN=C=N(CH₂)₃NMe₂ JACS 87 2492 (1965); 112 838, 4623, 5230, 8961 (1990); 113 297 (1991)
TL 32 5493 (1991)
- EtN=C=N(CH₂)₃NMe₂·HCl, DMAP TL 35 197 (1994)
- EtN=C=N(CH₂)₃NMe₂⁺ polymer TL 34 7685 (1993)
- EtN=C=N(CH₂)₃NMe₂, HOBT, (base) JACS 112 4011 (1990); 115 3420 (1993); 116 82 (1994)
TL 35 197 (1994)
JOC 60 3569 (1995)
- EtN=C=N(CH₂)₃NMe₂, HOAt JACS 115 4397 (1993)
JOC 59 929 (1994); 60 3569 (1995)
- EtN=C=N(CH₂)₃NMe₂,  JOC 60 3569 (1995)
- i*-PrN=C=N-*i*-Pr, HOBT TL 30 5045 (1989)
JACS 115 4419 (1993)
- , HOBT JOC 59 7503 (1994)
- CyN=C=NR JOC 21 439 (1956)
- DCC Chem Ind 1087 (1955)
JACS 77 1067 (1955); 78 1367 (1956); 111 6242 (1989)
Ber 92 2813 (1959)
Tetr 37 233 (1981) (review)
Chem Rev 81 589 (1981) (review)
JOC 52 5717 (1987)



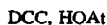
TL 27 841 (1980)
Pure Appl Chem 53 1141 (1981)



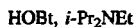
JACS 86 1839 (1964); 112 6696 (1990)
Int J Peptide Protein Res 17 197 (1981)
JCS Perkin I 2909 (1982)
Tetr 40 457 (1984)
JOC 57 1814 (1992); 60 6176 (1995)



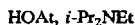
Ber 103 788 (1970)
TL 2695 (1974); 29 4225 (1988); 35 2279 (1994)
Int J Peptide Protein Res 17 197 (1981)
Tetr 40 457 (1984)
JACS 112 838, 7032 (1990); 114 6649, 10181 (1992); 116 82 (1994)
JOC 58 860, 2334 (1993)



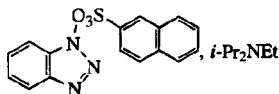
JACS 115 4397 (1993)
TL 35 2279 (1994)



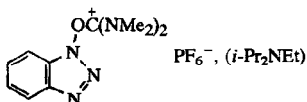
TL 35 2279 (1994)



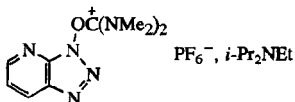
TL 35 2279 (1994)



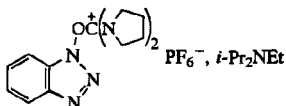
TL 35 9613 (1994)



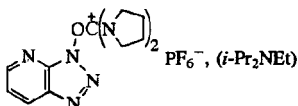
TL 30 1927 (1989); 35 2279 (1994)



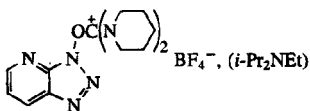
TL 35 2279 (1994)



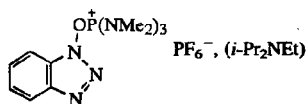
TL 33 647 (1992)



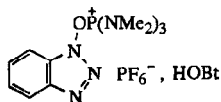
TL 34 4781 (1993); 35 2279 (1994)



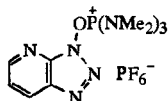
TL 34 4781 (1993)



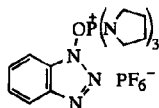
TL 1219 (1975)
 Tetr 36 3413 (1980); 44 675 (1988)
 JCS Perkin I 1025 (1985); 1915 (1987)
 JOC 53 617 (1988); 59 5192 (1994)
 JACS 112 7659 (1990); 113 5337, 8045 (1991)
 Int J Peptide Protein Res 31 86, 231 (1988);
 33 133 (1989)



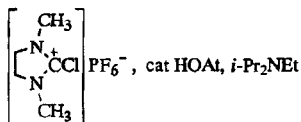
JOC 53 617 (1988)



TL 35 2279 (1994)



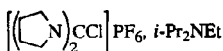
TL 31 205 (1990); 32 6387 (1991)



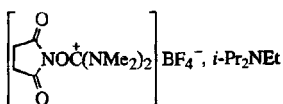
TL 35 3315 (1994)



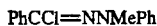
JACS 117 5401 (1995)



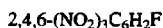
TL 32 1967 (1991)



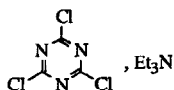
TL 32 1157 (1991)



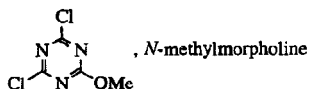
JACS 102 4537 (1980)



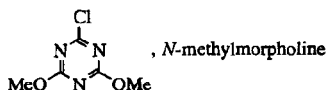
CL 647 (1977)
 BCSJ 51 1866 (1978)



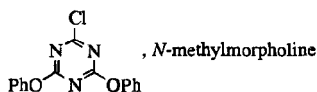
TL 3037 (1979)
 Ind J Chem B 20 852 (1981)



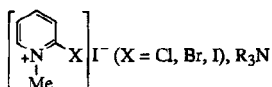
TL 26 2901 (1985)



TL 26 2901 (1985)
 JOC 60 7033 (1995)



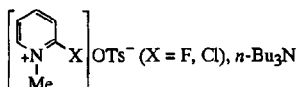
TL 26 2901 (1985)



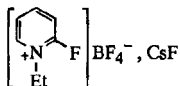
JCS 4650 (1964)

CL 1163 (1975)

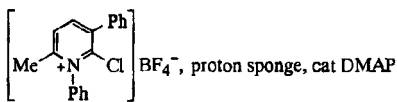
JACS 112 2998 (1990)



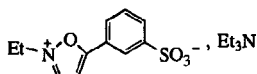
CL 57 (1976)



CL 391 (1980)

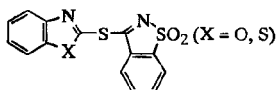


CL 1551 (1981)

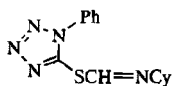


JACS 83 1010 (1961)

Org Syn Coll Vol 6 263 (1988)



Syn 933 (1982)

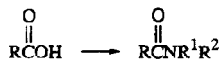


Angew Int 21 143 (1982)

lipases, molecular sieves

TL 32 2763 (1991)

For intramolecular reactions, see page 1861, Section 8.

 HCONH_2 , Δ ($\text{R}^1 = \text{R}^2 = \text{H}$)

JACS 71 2215 (1949)

 NH_2CONH_2 , Δ ($\text{R}^1 = \text{R}^2 = \text{H}$)

JACS 71 2215 (1949)

Org Syn Coll Vol 4 513 (1963)

 $\text{CH}_3\text{CONHCONH}_2$, Δ ($\text{R}^1 = \text{R}^2 = \text{H}$)

JACS 71 2215 (1949)

 $\text{R}^3\text{CONR}^1\text{R}^2$, H^+

JCS C 1337 (1967)

 $\text{R}^3\text{CONR}^1\text{R}^2$, AlCl_3

JCS C 1337 (1967)

JCS Perkin II 300 (1972)

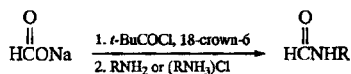
 R^1NCO ($\text{R}^2 = \text{H}$)

TL 27 1251 (1986)

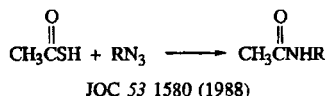
 $\text{R}^1\text{R}^2\text{NPOCl}_2$ ($\text{R}^1 = \text{R}^2 = \text{Me}$ or Et)

Syn Commun 9 31 (1979)

$(\text{Me}_2\text{N})_3\text{P}\cdot\text{I}_2$, HMPA ($\text{R}^1 = \text{R}^2 = \text{Me}$)	Austral J Chem 35 517 (1982)
R^1N_3 , $\text{P}(\text{OEt})_3$ ($\text{R}^2 = \text{H}$)	CC 776 (1984) (intramolecular)
R^1N_3 , Ph_2POEt ($\text{R}^2 = \text{H}$)	JOC 50 2601 (1985)
R^1N_3 , Ph_3P ($\text{R}^2 = \text{H}$)	TL 25 4841 (1984)
	JOC 50 2601 (1985)
R^1N_3 , Et_3P ($\text{R}^2 = \text{H}$)	TL 27 4623 (1986)
ArNO_2 , cat $\text{Ru}_3(\text{CO})_{12}$ ($\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Ar}$)	TL 32 4917 (1991)

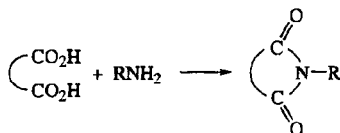


Recl J R Neth Chem Soc 101 460 (1982)



5. Carboxylic Acids to Imides

See also page 1990, Section 34.



Reagent(s)

Δ

HOAc

DCC, DMAP

Imide

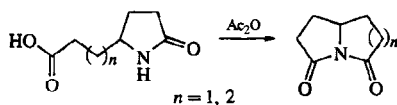
succinimide, glutarimide, maleimide JOC 54 4243 (1989); 55 5793 (1990); 60 7149 (1995)

phthalimide

SL 609 (1990)

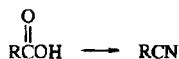
maleimide

TL 35 5555 (1994)



J Med Chem 30 498 (1987)
JOC 55 560 (1990)

6. Carboxylic Acids to Nitriles




NH_3 , silica gel

Org Syn Coll Vol 4 62 (1963)

NH_3 , ethyl polyphosphate

Syn 142 (1983)

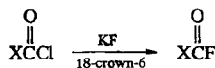
NH_2CONH_2	Org Syn Coll Vol 3 768 (1955)
ArCN (R = aryl)	JOC 23 1350 (1958)
$\text{NCCH}_2\text{CH}_2\text{CHMeCN}$, cat H_3PO_4	JOC 36 3050 (1971)
$\text{CH}_3\text{SO}_2\text{Cl}$, py/ NH_3 / $\text{CH}_3\text{SO}_2\text{Cl}$	Org Prep Proc Int 14 396 (1982)
$\text{ClSO}_2\text{NCO}/\text{DMF}$	Ber 100 2719 (1967) Tetr 24 1063 (1968) Org Syn 50 18 (1970) Syn Commun 12 25 (1982) Org Syn Coll Vol 6 304 (1988)
$\text{ClSO}_2\text{NCO}/\text{Et}_3\text{N}$	TL 1631 (1968)
PhSO_2NH_2	JCS 763 (1946)
TsNH_2 , TsOH	JCS 763 (1946)
TsNH_2 , PCl_5	Org Syn Coll Vol 3 646 (1955)
 NOH , $\text{DCC}/\text{RSO}_2\text{CN}$ (R = Me, <i>p</i> -Tol), $h\nu$	TL 32 3321 (1991)

7. Acid Halides to Other Acid Halides



<u>X</u>	<u>Reagent(s)</u>	
F	KF (freeze dried)	TL 30 1273 (1989)
	KF, $o\text{-C}_6\text{H}_4\text{Cl}_2$	JOC 56 900 (1991)
	KF, CH_3CN	CL 761 (1981)
	KF, CH_3CN , polyethylene glycol	CL 283 (1978)
	KF, cat 18-crown-6	JACS 96 2250 (1974)
		JOC 44 1016 (1979)
	KF, cat ($\text{Et}_3\text{NCH}_2\text{Ph}$)Cl	Syn Commun 12 513 (1982)
	KF, CF_3COCF_3	JOC 31 2316 (1966)
	KF, CaF_2 , sulfolane	CC 791 (1986)
	KF, cat (Ph_4P)Br, $o\text{-C}_6\text{H}_4(\text{COCl})_2$	CL 2213 (1989)
	KHF_2	Ber 89 862 (1956)
	py·(HF) _x	JOC 44 3872 (1979); 56 900 (1991)
	(Et_3NH)F	Bull Acad Sci USSR, Div Chem Sci 1269 (1963)
	<i>n</i> - Bu_4NF	JOC 49 3217 (1984)
	Na_2SiF_6	Angew 71 274 (1959)
	ZnF_2 , py	BCSJ 51 1267 (1978)
Br	KSO_2F	Ber 91 2553 (1958)
	R_2NSF_3	Syn 801 (1975)
	HBr	Ber 46 1417 (1913)
	Me_3SiBr	Syn 216 (1981)

I	HI	Ber 46 1417 (1913)
	NaI	JACS 55 374 (1933)
	NaI, CH ₃ CN	Chem Ind 1007 (1958)
	KI	Syn 715 (1981); 237 (1982)
	Me ₃ SiI	Ann Chem Pharm 3 267 (1832)
	H ₂ SiI ₂	Syn 216 (1981)
		JOC 55 3922 (1990)



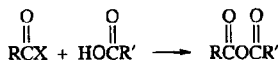
X = OR, NR₂

JOC 44 1016 (1979)

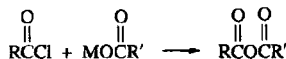
8. Acid Halides to Acid Anhydrides



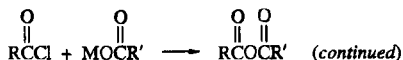
H ₂ O, py	JACS 71 2242 (1949)
H ₂ O, py, NaHCO ₃ (R = Ar)	Angew Int 7 465 (1968)
H ₂ O, Cl ₃ CCOCF ₃ /py	JOC 51 3390 (1986)
py/H ₂ O	Org Syn Coll Vol 3 28 (1955)
Ac ₂ O	Helv 9 177 (1926)
	J Am Oil Chem Soc 31 151 (1954)
	JOC 24 388 (1959)



R ₃ N	Org Syn 26 1 (1946)
	JCS 2117 (1953)
	Org Syn Coll Vol 3 28 (1955)
	CL 145 (1979)
	TL 27 4933 (1986); 28 4711 (1987)
	JOC 58 2128 (1993)
CoCl ₂	TL 33 593 (1992)



<u>M</u>	
Na	JACS 73 4911 (1951)
	JCS 755 (1964)
	Rec Trav Chim 85 627 (1966)
	Org Syn 50 1 (1970)
	Org Syn Coll Vol 6 8 (1988)

M

K

Ti

Ag

JACS 61 684 (1939); 69 2231 (1947)

JACS 90 2422 (1968)

JACS 75 232 (1953)

9. Acid Halides to Esters



ROH

Org Syn Coll Vol 5 1 (1973)

JACS 108 468 (1986)

ROH, Me₃N or EtNMe₂

JACS 111 7650 (1989) (asymmetric)

TL 33 6799 (1992)

ROH, Et₃N

Org Syn Coll Vol 5 258 (1973)

ROH, PhNMe₂

JACS 54 2088 (1932); 65 986 (1943)

Org Syn Coll Vol 3 142 (1955); 5 171 (1973);
8 522 (1993)

ROH, py

JACS 73 5487 (1951); 109 6726, 7838 (1987);
112 6608 (1990)

JOC 21 1362 (1956)

ROH (diol), 2,6-dimethoxypyridine (on chiral RCOI;
enantioselective)

SL 611 (1994)

ROH, DMAP

Angew Int 17 569 (1978)

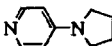
Tetr 34 2069 (1978)

JACS 107 3279 (1985); 109 6726 (1987)

JOC 50 2390 (1985)

TL 31 1517 (1990)

Org Syn Coll Vol 8 516 (1993)

ROH, 

Angew Int 17 569 (1978)

Tetr 34 2069 (1978)

ROH, Mg

Org Syn Coll Vol 3 144 (1955)

LiOR

JOC 35 1198 (1970); 52 2927 (1987)

Org Syn 51 96 (1974)

Org Syn Coll Vol 6 259 (1988)

TL 35 5543 (1994)

LiOC≡CR

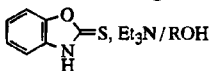
TL 34 1461 (1993)

NaOAr

Org Syn Coll Vol 7 190 (1990)

TIS-*t*-Bu / ROH, Hg(O₂CCF₃)₂

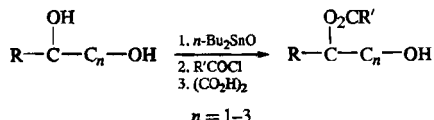
JACS 97 3515 (1975)



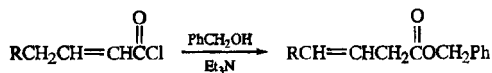
Syn 991 (1981)

**Reagents**

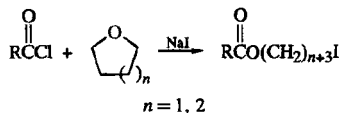
	η	
AcCl, 2,4,6-collidine or <i>i</i> -Pr ₂ NEt	1-3	JOC 58 3791 (1993)
<i>n</i> -Bu ₂ Sn(OMe) ₂ / R'COCl	1	SL 913 (1993)
<i>n</i> -Bu ₂ SnO / R'COCl	1, 2	Tetr 41 643 (1985) (review) SL 89 (1994)
cat <i>n</i> -Bu ₂ SnO, R'COCl, Et ₃ N, ultrasound	1	SL 455 (1995)



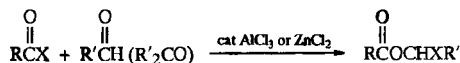
JOC 55 5132 (1990)



SL 1131 (1995)



TL 23 681 (1982)

 $\text{X} = \text{Cl}, \text{Br}$

Helv 54 1037 (1971); 60 1061 (1977); 61 2047 (1978)

Syn 593 (1978)

JOC 58 588 (1993)

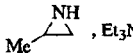

H₂, cat HRuCl(PPh₃)₃ or RuCl₂(PPh₃)₃,
2,4,6-collidine

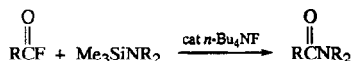
JOC 56 5159 (1991)

LiInH₄

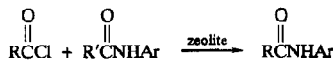
TL 36 3169 (1995)

10. Acid Halides to Amides

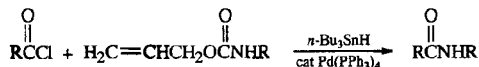
NH_3	JACS 71 2215 (1949) Org Syn Coll Vol 3 490 (1955)
$\text{R}'\text{NH}_2$	JOC 59 3642 (1994)
$\text{R}'_2\text{NH}$	JACS 71 2215 (1949); 108 1039 (1986) Org Syn Coll Vol 4 339 (1963); 5 387 (1973) JOC 54 150 (1989); 58 4043 (1993)
$\text{R}'_2\text{NH}, \text{HCl}$	JACS 114 3028 (1992)
$\text{R}'_2\text{NH}, \text{NaOH}$	Org Syn Coll Vol 1 99 (1941)
$\text{R}'_2\text{NH}, \text{Et}_3\text{N}$	JACS 110 6528 (1988)
 , Et_3N	TL 35 5073 (1994)
$\text{R}'_2\text{NH}, \text{Et}_3\text{N}, \text{cat DMAP}$	JACS 113 7666 (1991)
$\text{RCH}_2\text{NR}'_2$	Org Rxn 39 85 (1990) (review)
 , $\text{Et}_3\text{N}/\text{R}'_2\text{NH}$	Syn 991 (1981)
polymer-ArOH, py/ $\text{R}'_2\text{NH}$	Syn Commun 12 709 (1982)



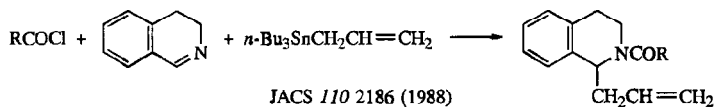
TL 28 5099 (1987)



TL 35 8877 (1994)

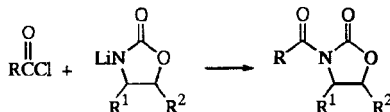


JOC 60 1733 (1995)



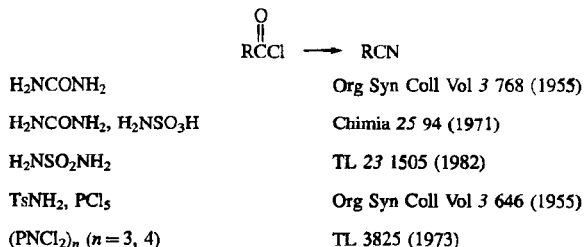
JACS 110 2186 (1988)

11. Acid Halides to Imides

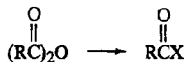


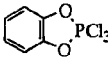
See page 1990, Section 34.

12. Acid Halides to Nitriles



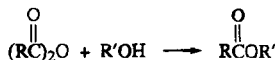
13. Acid Anhydrides to Acid Halides



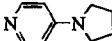
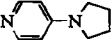
<u>X</u>	<u>Reagent</u>	
F	$\text{HF}\cdot\text{py}$ $\text{SeF}_4\cdot\text{py}$	JOC 44 3872 (1979) JACS 96 925 (1974)
Cl	PCl_5 	Org Syn Coll Vol 2 528 (1943) Ber 96 1387 (1963) Z Chem 22 126 (1982) (review)
I	Me_3SiI H_2SiI_2 $\text{H}_2\text{SiI}_2, \text{I}_2$ P, I_2	JOC 55 3922 (1990) JOC 55 3922 (1990) JOC 55 3922 (1990) Ann 103 335 (1857); 104 111 (1857)

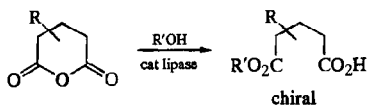
14. Acid Anhydrides to Esters

For the reduction of cyclic anhydrides to lactones, see page 1677, Section 2.

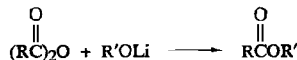


Δ	Org Syn Coll Vol 3 169 (1955) TL 32 5077 (1991)
lipase (enantioselective)	JOC 53 5531 (1988); 57 5231, 6003 (1992); 58 1054 (1993); 59 3433 (1994) TL 30 1555, 3817 (1989); 31 3405, 4875 (1990); 33 1911, 2327, 2469, 6283, 6287, 6967 (1992); 35 421 (1994); 36 505 (1995) Tetr Asym 2 1 (1992) (<i>Pseudomonas fluorescens</i> review)

TsOH	Org Syn Coll Vol 4 304 (1963); 8 141 (1993)
TsOH, RCO ₂ H	JACS 75 3489 (1953)
cat COCl ₂	CC 114 (1987) JOC 57 2001 (1992)
Mg, Zn or ZnCl ₂	JACS 54 2088 (1932)
cat BF ₃ ·OEt ₂	Chem Pharm Bull 29 3202 (1981)
Me ₃ SiCl	TL 24 1189 (1983) JOC 52 3034 (1987)
cat Sc(OTf) ₃	JACS 117 4413 (1995)
ZnCl ₂	Org Syn Coll Vol 3 141 (1955)
NaOAc	Ber 58 666 (1925) Org Syn Coll Vol 1 285 (1941)
Cy ₂ NH	SL 105 (1994)
Et ₃ N, cat DMAP	JOC 59 5078 (1994)
py	JACS 109 7838 (1987)
DMAP	Angew Int 8 981 (1969); 17 569 (1978) Syn 619 (1972) JOC 52 4495 (1987); 53 2374 (1988); 58 142 (1993)
DMAP, py	TL 30 5045 (1989)
DMAP, py, pressure	SL 650 (1995)
cat DMAP, Et ₃ N	Angew Int 8 981 (1969); 17 569 (1978) Syn 619 (1972) JACS 108 4603 (1986)
cat DMAP, py	JOC 52 3784 (1987)
	Syn 619 (1972)
cat  , Et ₃ N	Tetr 34 2069 (1978)
cat cinchonine alkaloid (enantioselective)	JCS Perkin I 1053 (1987) SL 151 (1992)
cat <i>n</i> -Bu ₃ P, (Et ₃ N)	JACS 115 3358 (1993) JOC 58 7286 (1993)



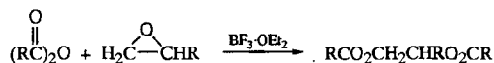
TL 29 1717 (1988)



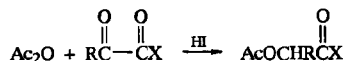
JOC 56 2122 (1991); 59 7849 (1994) (chiral)



TL 34 7565 (1993)

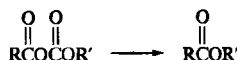


JOC 53 5547 (1988)



X = R, OR

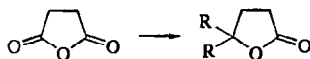
JOC 55 1354 (1990)

Et₃N, cat DMAP

JOC 50 560 (1985)

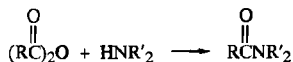
cat *n*-Bu₃P

JOC 58 7286 (1993)



See page 1861, Section 8.

15. Acid Anhydrides to Amides



Org Syn Coll Vol 2 11 (1943)

JOC 53 929 (1988); 58 6625 (1993)

SL 151 (1992)

Et₃N

SL 639 (1995)

py

Org Syn Coll Vol 4 5 (1963)

NaOH

JACS 114 3028 (1992)

RCO₂H, H₂O

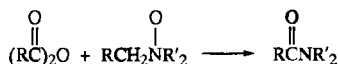
Org Syn Coll Vol 3 661 (1955)

polymer-ArOH, py

Syn Commun 12 709 (1982)

cat CoCl₂

CC 114 (1987)



Org Rxn 39 85 (1990) (review)



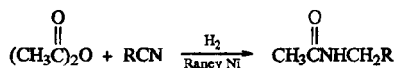
See page 1978, Section 25.



JOC 60 1733 (1995)

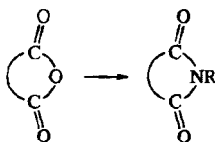


JOC 56 2122 (1991); 60 6277 (1995)



JOC 53 2847 (1988)

16. Acid Anhydrides to Imides

 NH_3

JOC 60 7186 (1995)

 $(\text{Me}_3\text{Si})_2\text{NH}$, MeOH

TL 31 5201 (1990)

 RNH_2 JOC 54 4243 (1989); 55 215 (1990); 59 2813 (1994)
SL 63 (1994) RNH_2 , Et_3N

JOC 54 4243 (1989); 59 6911 (1994)

 RNH_2 /EtN=C=N(CH₂)₃NMe₂/HOBt

JOC 56 5893 (1991)

 RNH_2 /DCC

Syn 819 (1991)

 RNH_2 /DCC, HOBT

Syn 484 (1973)

 RNH_2 /NaOAc, Ac₂OJOC 25 1012 (1960); 54 2502 (1989); 56 5893
(1991); 60 6114 (1995)
JACS 112 8100 (1990) $(\text{NH}_4)\text{OAc}$ or $(\text{MeNH}_3)\text{OAc}$, HOAc

JCS Perkin I 2567 (1993)

 RNH_2 /

JOC 55 215 (1990)

 RNH_2 /(COCl)₂

SL 979 (1992)

17. Esters to Carboxylic Acids



Reviews:

- Org Rxn 24 187 (1976) (S_N2-type)
 Tetr 36 2409 (1980); 49 3691 (1993)
 Ann Rep Med Chem 19 263 (1984) (enzymes)
 Angew Int 24 617 (1985) (enzymes)
 "Preparative Biotransformations", Ed. S. M. Roberts, J. Wiley, New York (1992) (enzymes)
 Pure Appl Chem 64 1085, 1129, 1165 (1992) (all enzymes)

- | | |
|--|---|
| acetyl esterase | SL 65 (1994) |
| acetylcholine esterase (enantioselective) | JOC 57 1588 (1992) |
| cholesterol esterase (enantioselective) | JOC 52 1765, 2608 (1987); 56 2656 (1991)
TL 30 1617 (1989)
JACS 117 5677 (1995) |
| horse liver esterase (enantioselective) | TL 29 1915 (1988) (lactones); 30 67 (lactones), 7053 (1989); 31 653 (1990) |
| pig liver esterase (enantioselective) | JACS 104 7294 (1982); 106 3695 (1984); 108 4603 (1986); 110 4409 (1988); 112 1164, 4946 (1990)
Helv 66 2501 (1983)
Angew Int 23 64, 66, 67 (1984)
CC 236 (1984); 808, 1545 (allenic esters) (1986); 1041 (1987) (diester)
TL 26 2073, 4957, 5831 (1985); 27 2543, 4639 (1986); 28 781, 1887, 2767, 3103, 4661 (1987); 29 1915 (lactones), 2563, 2697 (bicyclic esters), 3951 (glutarates) (1988); 30 2513, 3201 (1989); 31 653 (1990); 33 1081, 2871 (1992); 35 7949 (1994)
JOC 51 1003, 2047 (1986); 52 4565 (1987); 53 937, 1567, 2637 (1988); 54 2787, 5115 (1989); 55 5878 (1990) (α-hydroxy esters); 56 3869, 5375, 7251 (1991); 57 3463, 4746, 5005, 5563 (1992); 58 802, 1882, 4819 (1993); 60 8110 (1995)
Bioorg Chem 14 176 (1986)
Chimia 40 314 (1986)
Ann 687 (1986)
Org Rxn 37 1 (1989) (review)
Pure Appl Chem 64 1187 (1992) (review)
Org Syn Coll Vol 8 332 (1993)
SL 127 (1994) |
| pig liver esterase-polyethylene glycol monomethyl ether (enantioselective) | TL 36 3833 (1995) |
| bovine liver acetone powder (enantioselective) | Pure Appl Chem 64 1067 (1992) |

chicken liver acetone powder (enantioselective)	Pure Appl Chem 64 1067 (1992)
goat liver acetone powder (enantioselective)	Pure Appl Chem 64 1067 (1992)
pig liver acetone powder (enantioselective)	TL 31 4347 (1990) Pure Appl Chem 64 1067 (1992)
rabbit liver esterase (enantioselective)	TL 33 5901 (1992)
various proteases (enantioselective)	TL 34 3441 (1993); 35 1673 (1994)
α -lytic protease (enantioselective)	JACS 110 7236 (1988)
protease subtilisin (enantioselective)	JACS 108 2767 (1986) TL 28 5169 (1987)
subtilisin A (enantioselective)	JOC 58 7263 (1993)
subtilisin BPN' (enantioselective)	JACS 110 7236 (1988)
subtilisin Carlsberg (enantioselective)	JACS 110 7236 (1988) TL 31 4883 (1990); 34 435, 4485 (1993) JOC 60 2292 (1995)
subtilisin 8350 (enantioselective)	JACS 112 945 (1990)
elastase (enantioselective)	JACS 110 7236 (1988)
various cellulases (enantioselective)	JOC 51 1003 (1986)
pig pancreatic lipase (enantioselective)	TL 29 1915 (1988) (lactones); 30 2697, 3201, 5319 (1989); 32 3043 (1991) JOC 57 1540 (1992)
porcine pancreatic lipase (enantioselective)	JACS 106 3695, 7250 (epoxy esters) (1984); 108 4603 (1986); 109 2845 (1987); 112 1164 (1990) CC 1563 (1985); 1298 (1986); 1080 (1987) TL 26 2073 (1985); 27 5707 (1986); 28 531, 1973, 2767, 2989, 3471, 4661, 4669 (1987); 29 2455 (1988); 30 261, 1793 (1989); 31 2037 (lactones), 3283, 4827 (1990); 32 5683 (1991); 33 1399, 2145 (1992); 34 4215, 8549 (1993); 36 6499 (1995) (1,3-dioxolan-2-ones) JOC 51 1003 (1986); 52 1765 (1987); 53 4939 (1988); 56 5375 (1991); 58 802 (1993)
porcine pancreatic lipase, ultrasound (enantioselective)	TL 36 6067 (1995)
lipase A6 (enantioselective)	JOC 56 797 (1991)
lipase Amano A or Amano A-6 (enantioselective)	TL 27 5241 (1986)
lipase Amano AK (enantioselective)	TL 29 4927 (1988) JOC 58 1068, 6486 (1993)
lipase Amano K-10 (enantioselective)	TL 29 4927 (1988) JOC 58 1068 (1993)
lipase Amano LPL-80 (enantioselective)	JOC 57 4544 (1992) TL 36 6987 (1995)

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| lipase Amano LP-80 (enantioselective) | JACS 111 3924 (1989)
JOC 55 4897 (1990) |
| lipase Amano N | TL 34 3111 (1993) |
| lipase Amano P (enantioselective) | JOC 52 5079 (1987); 56 1521 (1991); 57 5231 (1992); 58 3980 (1993)
TL 30 3777 (1989); 31 3011 (1990) |
| lipase Amano PS-30 (enantioselective) | SL 813 (1992)
JOC 52 4289 (1992); 58 2714 (1993); 60 6674 (1995)
TL 35 5205 (1994) |
| lipase Amano PS-800 (enantioselective) | TL 34 6517 (1993) |
| lipase-MY (enantioselective) | JOC 52 3211 (1987) (trifluoromethyl carbinol esters) |
| lipase Novo SP 435 (enantioselective) | SL 813 (1992) |
| lipase OF (enantioselective) | TL 32 3529 (1991) |
| lipase P-30 (enantioselective) | TL 32 3941 (1991)
JOC 56 6538 (1991); 58 1068 (1993)
JACS 115 49 (1993)
Org Syn Coll Vol 8 258 (1993) |
| lipase PS (enantioselective) | JOC 59 7027, 7214 (1994) |
| lipase SAM-II (enantioselective) | TL 33 6335 (1992) |
| various lipases (enantioselective) | JOC 55 6252 (1990)
TL 35 1673, 4635 (1994) |
| various lipases on Celite (enantioselective) | TL 29 567 (1988) |
| antibodies (enantioselective) | JACS 111 5961 (1989); 113 2123 (1991) |
| baker's yeast (enantioselective) | TL 27 4293 (1986)
JOC 54 3218 (1989)
Chem Rev 91 49 (1991) (review) |
| α -chymotrypsin (enantioselective) | JACS 83 4228 (1961); 90 3495 (1968); 108 2767 (1986); 110 7236 (1988)
JOC 49 3657 (1984); 51 1003 (1986); 53 1567 (1988); 58 683 (1993)
TL 26 4957 (1985); 28 4661, 4935 (1987); 32 4249 (1991); 34 435 (1993); 35 4635 (1994)
SL 448 (1990); 127 (1994) |
| pancreatin (enantioselective) | Agric Biol Chem 46 1593 (1982)
JOC 52 5079 (1987) |
| penicillin acylase (enantioselective) | TL 30 3057 (1989) |
| steapsin (enantioselective) | Agric Biol Chem 46 1593 (1982)
JOC 52 5079 (1987); 53 104 (1988)
TL 28 2767 (1987); 33 6335 (1992) |

thermitase (R = <i>t</i> -Bu)	SL 37 (1992)
trypsin (enantioselective)	JACS 110 7236 (1988)
various enzymes (enantioselective)	TL 31 445 (1990)
other microbiological reagents (enantioselective)	Agric Biol Chem 37 1687 (1973) TL 25 5235 (1984)
<i>Aspergillus niger</i> (enantioselective)	JOC 51 1003 (1986); 53 4939 (1988); 59 2075 (1994) TL 27 5203 (1986); 34 7767 (1993)
<i>Aspergillus oryzae</i> (enantioselective)	JACS 109 2845 (1987)
<i>Aspergillus saitoi</i> (enantioselective)	JACS 109 2845 (1987)
<i>Bacillus subtilis</i> (enantioselective)	Agric Biol Chem 37 1687, 1691, 1695 (1973); 38 1961, 1965 (1974); 39 89 (1975) Tetr 36 91 (1980) JACS 108 4603 (1986); 109 2845 (1987) TL 30 2555, 3819 (1989)
<i>Candida antarctica</i> (enantioselective)	TL 33 7287 (1992)
<i>Candida cylindracea</i> lipase (enantioselective)	JOC 51 1003 (1986); 52 1765 (1987); 53 4939 (1988); 55 1749, 4643 (1990); 57 5931, 6635 (1992); 58 4010 (1993); 59 6018 (1994) JACS 108 6421 (1986); 109 2845 (1987); 111 6836 (1989) (inhibition); 112 1164, 1990 (1990) TL 27 2843 (1986); 28 2767, 2989, 4661 (1987); 29 1903 (1988); 30 3201, 5319 (1989); 31 3011, 3283, 4827, 6797, 7159, 7163 (1990); 32 5683 (1991); 33 2145 (1992); 35 2611 (1994)
<i>Candida lipolytica</i> (enantioselective)	JOC 57 3525 (1992)
<i>Candida rugosa</i> lipase (enantioselective)	JOC 56 2656 (1991); 60 212 (1995) TL 32 6763 (1991) JACS 116 3180 (1994); 117 6845 (1995)
<i>Chromobacterium violaceum</i> (enantioselective)	TL 27 5203 (1986)
<i>Chromobacterium viscosum</i> (enantioselective)	CC 1298 (1986) JOC 51 1003 (1986)
<i>Corynebacterium equi</i> (IFO 3730) bacterinm (enantioselective)	TL 25 5235 (1984); 28 1303 (1987) (α -benzyloxy esters) CL 217 (1986) (2- and 3-arylsulfinyl esters)
<i>Fusarium solani pisi</i> cutinase (enantioselective)	SL 243 (1992)
<i>Gliocladium roseum</i> (enantioselective)	JACS 108 4603 (1986)
<i>Humicola lanuginosa</i> (enantioselective)	TL 32 6763 (1991)
<i>Mucor meihei</i> lipase (enantioselective)	CC 1298 (1986) TL 27 5203 (1986) JACS 109 2845 (1987)

<i>Pseudomonas</i> K-10 (enantioselective)	TL 30 3633 (1989) JOC 57 1290 (1992) (both α -sulfinyl)
<i>Pseudomonas cepacia</i> (enantioselective)	JOC 56 2656, 7251 (1991); 57 5776 (1992); 58 1054, 4346 (1993); 59 7014 (1994); 60 615, 6959 (1995) TL 33 7157 (1992); 36 1063, 4865 (1995)
<i>Pseudomonas fluorescens</i> lipase (enantioselective)	CC 838 (1987) TL 30 3819 (1989); 32 5805 (1991); 33 2145 (1992); 34 3785 (1993); 35 1415 (1994) JOC 55 812, 1749, 3670 (1990); 58 802, 3980 (1993) Org Syn 69 1 (1990) Tetr Asym 2 733 (1991) (review) Org Syn Coll Vol 8 516 (1993)
<i>Pseudomonas fragi</i> (enantioselective)	TL 32 5805 (1991)
<i>Pseudomonas</i> sp. lipase (enantioselective)	TL 27 5203 (1986); 30 1793 (1989); 31 3011, 3287, 4827, 6387, 6407, 6797 (1990); 33 7157 (1992); 34 2617 (1993); 35 1019 (1994) CC 1298 (1986) JACS 109 2845 (1987)
<i>Rhizopus arrhizus</i> lipase (enantioselective)	TL 27 5203 (1986); 28 2767 (1987); 32 1331 (1991)
<i>Rhizopus nigricans</i> mold (enantioselective)	JOC 48 3017 (1983); 49 675 (1984); 52 2400 (1987)
<i>Rhizopus niveus</i> lipase (enantioselective)	TL 27 5203 (1986) SL 105 (1990)
<i>Saccharomyces</i> sp. (enantioselective)	Biochim Biophys Acta 376 363 (1973)
<i>Streptomyces griseus</i> (enantioselective)	JACS 109 2845 (1987)
<i>Trichoderma</i> S (enantioselective)	Agric Biol Chem 37 1687, 1691, 1695 (1973); 38 1961, 1965 (1974); 39 89 (1975)
<i>Trichoderma viride</i> (enantioselective)	Agric Biol Chem 37 1687 (1973) JOC 51 1003 (1986)
H ₂ O (R = CF ₃)	JOC 57 4749 (1992)
HCl	JACS 73 4752 (1951); 87 3089 (1959) (both R = <i>t</i> -Bu) JCS C 1191 (1966) (R = Ph ₂ CH)
HCl, PhOH (R = benzylic)	JOC 56 3633 (1991)
HCl, HBr or H ₂ SO ₄ (phase transfer) (R = 1° alkyl, <i>t</i> -Bu)	JOC 47 154 (1982)
HBr (R = Ph ₂ CH)	JCS C 1191 (1966)
HCO ₂ H (R = Ph ₂ CH)	Chem Pharm Bull 30 4545 (1982)
HCO ₂ H, cat MeSO ₃ H	Chem Ind 193 (1964)
CF ₃ CO ₂ H	JCS C 1191 (1966) (R = Ph ₂ CH) JACS 99 2353 (1977) (R = <i>t</i> -Bu, Ph ₂ CH) Syn Commun 12 855 (1982) (R = Me)

	JOC 54 3754 (1989) (R = <i>t</i> -Bu); 55 1169 (R = <i>t</i> -Bu), 4657 (R = Ph ₂ CH) (1990); 59 929 (1994) (R = <i>t</i> -Bu) TL 35 1651 (1994) (R = 4-MeOC ₆ H ₄ CHCH ₃)
CF ₃ CO ₂ H, PhOH (R = benzylic, <i>t</i> -Bu)	TL 31 6661 (1990) JOC 56 3633 (1991)
CF ₃ CO ₂ H, Et ₃ SiH (R = <i>t</i> -Bu)	TL 33 5441 (1992)
Cl ₂ CHCO ₂ H (R = <i>p</i> -MeOC ₆ H ₄ CHCH ₃)	TL 35 1651 (1994)
Li, NH ₃ (R = Me)	JACS 80 217 (1958)
Mg, MeOH (R = 1°, 2°, 3° alkyl; benzylic)	TL 35 6207 (1994)
cat Pd, H ₂ (R = benzylic)	Org Rxs 7 263 (1953) (review) JCS C 1191 (1966)
cat Pd-C, H ₂ (R = benzylic)	Helv 31 439 (1948) Org Rxs 7 263 (1953) (review) J Med Chem 18 403 (1975) Chem Pharm Bull 26 2269 (1978) JACS 114 6227 (1992) JOC 58 142 (1993)
cat Pd-C, (NH ₄)O ₂ CH (R = CH ₂ Ph)	Syn 929 (1980)
cat Pd-C, 1,4-cyclohexadiene, MeOH or EtOH (R = benzylic)	TL 28 3225 (1987); 33 2299 (1992)
cat Pd(OAc) ₂ , cat P(OEt) ₃ , cat dimedone, NaHCO ₃ (R = allyl)	SL 609 (1995)
cat PdCl ₂ (PPh ₃) ₂ , (NH ₄)O ₂ CH (R = allylic)	TL 613 (1979)
cat Pd ₂ (DBA) ₃ , HCO ₂ H, Et ₃ N, cat PPh ₃ (R = allyl)	JOC 59 3113 (1994)
cat Pd(PPh ₃) ₄ , (NH ₄)OAc (R = allyl)	JACS 111 8036 (1989)
cat Pd(PPh ₃) ₄ , NaO ₂ CCH ₂ Et(CH ₂) ₃ CH ₃ (R = allylic)	JOC 57 4352 (1992)
cat Pd(PPh ₃) ₄ -PPh ₃ , KO ₂ CCH ₂ Et(CH ₂) ₃ CH ₃ (R = allylic)	JOC 47 587 (1982)
cat Pd(PPh ₃) ₄ , R ₂ NH (R = allylic)	Angew Int 23 71 (1984) TL 28 4371 (1987); 32 4207 (1991) JOC 54 751 (1989) JACS 117 2479 (1995)
cat Pd(PPh ₃) ₄ , PhCH ₂ ONH ₂ (R = allyl)	JOC 58 618 (1993)
cat Pd(PPh ₃) ₄ , PhSiH ₃ (R = allylic)	TL 36 5741 (1995)
cat Pd(PPh ₃) ₄ , Ph ₂ SiH ₂ (R = allylic)	Israel J Chem 24 82 (1984)
cat Pd(PPh ₃) ₄ , Me ₃ SiO(MeSiHO) ₄₀ SiMe ₃ (R = allylic)	Israel J Chem 24 82 (1984)
cat Pd(PPh ₃) ₄ , Me ₃ SiN ₃ , <i>n</i> -Bu ₄ NF (R = allylic)	TL 35 5421 (1994)
cat Pd(PPh ₃) ₄ , CF ₃ CON(Me)SiMe ₃ (R = allylic)	TL 36 5741 (1995)

Zn (R = CH ₂ CCl ₃)	Syn 457 (1976) JOC 52 1790 (1987); 58 3538 (1993)
Zn, sonication (R = CH ₂ CCl ₃)	JACS 117 2479 (1995)
Zn, H ₂ O, HOAc (R = CH ₂ CCl ₃)	JACS 88 852 (1966)
Zn, MeOH (R = aryl)	TL 22 335 (1981)
Zn, HOAc (R = <i>p</i> -NO ₂ C ₆ H ₄ CH ₂)	Chem Pharm Bull 26 2269 (1978)
Zn, HCl (R = <i>p</i> -NO ₂ C ₆ H ₄ CH ₂)	J Med Chem 18 403 (1975)
Zn, py, CH ₃ COCH ₂ COCH ₃ (R = CH ₂ COPh)	TL 31 6539 (1990)
Cd, HOAc (R = CH ₂ CCl ₃)	TL 23 249 (1982); 35 7747 (1994)
Sm, I ₂ , MeOH (R = 1°, 2° alkyl; benzylic; aryl)	SL 1261 (1995)
SmI ₂ [R = CH ₂ CH ₂ Br(I)]	JOC 59 2257, 2304 (1994)
M ₂ CO ₃ (M = Na, K, Rb or Cs), MeOH, H ₂ O (R = Me, Et, PhCH ₂)	TL 32 327 (1991)
K ₂ CO ₃ (R = CH ₂ CH ₂ CN)	TL 30 3569 (1989)
LiOH/H ₃ O ⁺	JCS 6655 (1965) JACS 108 4603 (1986); 117 2479, 2533 (1995)
NaOH/H ₃ O ⁺	JACS 58 1014 (1936); 109 6726 (1987); 117 2533 (1995) Org Syn Coll Vol 1 379, 391 (1941); 3 526, 531, 652 (1955); 4 582, 616, 628 (1963); 8 516 (1993) Tetr 6 253 (1959) JOC 50 2128 (1985) TL 31 3687 (1990) (lactone)
KOH/H ₃ O ⁺	Org Syn Coll Vol 3 267 (1955); 4 608, 633 (1963); 8 522 (1993) JOC 52 4647 (1987)
anhydrous KOH/H ₃ O ⁺	TL 35 8931 (1994)
KOH, Al ₂ O ₃ /H ₃ O ⁺	Syn Commun 11 413 (1981)
Ba(OH) ₂ /H ₃ O ⁺	Org Syn Coll Vol 4 635 (1963)
Al ₂ O ₃ , microwave irradiation	SL 793 (1993) TL 34 4603 (1993)
H ₂ O ₂ , LiOH	JOC 54 3988 (1989) TL 34 6969 (1993)
H ₂ O ₂ , NaHCO ₃	TL 36 2001 (1995)
NaO ₂ , DMSO (R = Me)	JOC 44 4727 (1979)
KO- <i>t</i> -Bu, DMSO (R = Me)	TL 2969 (1964)
2 KO- <i>t</i> -Bu, 1 H ₂ O (R = 1°, 3° alkyl)	JOC 42 918 (1977); 59 2577 (1994) TL 28 1131 (1987)
Na ₂ S, H ₂ O (R = <i>p</i> -NO ₂ C ₆ H ₄ CH ₂)	JOC 43 1243 (1982)
Na ₂ S, CH ₃ CN [R = (CH ₂) _n Cl; n = 4, 5]	Syn Commun 4 307 (1974)

KSCN, DMF (R = Me, PhCH ₂)	JOC 37 744 (1972) Syn Commun 5 305 (1975)
PhCH ₂ SH, <i>n</i> -Bu ₄ NF· <i>x</i> H ₂ O (R = CHPhCOPh)	TL 34 2783 (1993)
EtSH, AlX ₃ (X = Cl, Br) (R = Me, PhCH ₂)	TL 5211 (1978) JOC 46 1991 (1981)
Me ₂ S or tetrahydrothiophene, AlX ₃ (X = Cl, Br) (R = Me, Et, <i>n</i> -Pr, <i>i</i> -Pr)	JOC 46 1991 (1981); 50 3957 (1985)
LiSMe (R = Me or lactone)	TL 3859 (1977) JACS 102 3904 (1980)
LiS- <i>n</i> -Pr, HMPA (R = Me)	TL 4459 (1970) JACS 106 5304 (1984); 113 5337 (1991) JOC 52 4634 (1987)
NaSMe (R = 9-anthrylmethyl, lactone)	Ber 83 265 (1950) JACS 96 590 (1974)
NaSEt, DMF (R = Me)	Austral J Chem 25 1731 (1972)
NaS- <i>n</i> -Pr, DMF (R = Me, Et, PhCH ₂)	JOC 27 739 (1962)
NaSPh, DMF (R = Me, benzylic, phenacyl)	JOC 29 2006 (1964)
(NaSCH ₂) ₂ , CH ₃ CN [R = CH ₂ CH ₂ Cl(Br)]	Syn 510 (1975)
Na ₂ CS ₃ , CH ₃ CN [R = CH ₂ CH ₂ Cl(Br)]	Syn 715 (1974)
Me ₂ Sn(SMe) ₂ , BF ₃ ·OEt ₂ , HOAc (R = CHMeCH=CHPh)	TL 30 2959 (1989)
Na ₂ S ₂ O ₄ , H ₂ O, Na ₂ CO ₃ (R = <i>p</i> -NO ₂ C ₆ H ₄ CH ₂)	Syn Commun 12 219 (1982)
KSeO ₃ K (lactone)	JOC 31 1202 (1966)
LiSeCH ₃ , DMF (R = Me, Et, <i>i</i> -Pr; R' = Ph)	Syn Commun 13 617 (1983)
NaSeCH ₃ , DMF (R = Me)	TL 28 4225 (1987)
NaSeCH ₂ Ph (lactones)	Arkiv Kemi 24 415, 573 (1965)
NaSePh (R = 1°, 2° alkyl; benzylic; lactone)	Coll Czech Chem Commun 34 3801 (1969) TL 4365, 4369 (1977) JACS 102 3904 (1980) JOC 46 2605 (1981); 54 1483 (1989)
Me ₃ SiSePh, KF, 18-crown-6 (R = Et, lactone)	TL 5087 (1978)
<i>i</i> -Pr ₂ NEt or <i>N</i> -methylmorpholine, H ₂ O, CH ₃ CN, high pressure (R = Me, Et, benzylic)	JOC 56 5737 (1991)
Me ₂ NCH ₂ CONMeOH (R = aryl)	TL 30 207 (1989)
NaCN, HMPA (R = Me)	TL 3565 (1973)
NBS, cat (PhCO ₂) ₂ /H ₂ O (R = PhCH ₂)	SL 219 (1994)
I ₂ (R = CH ₂ CH=CHMe ₂)	TL 35 1539 (1994)
<i>n</i> -Bu ₄ NF (R = <i>p</i> -NO ₂ C ₆ H ₄ CH ₂ , Cl ₃ CCH ₂ and PhCOCH ₂ esters of amino acids)	JOC 56 5464 (1991)

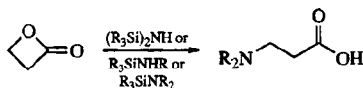
LiBr, DMF (R = Me)	JCS 6655 (1965)
LiI, EtOAc (R = Me, <i>t</i> -Bu, ArCH ₂ ; α -acylamino and α -alkoxycarbonylamino esters)	TL 35 2505 (1994)
LiI, DMF (R = Me)	JCS 6655 (1965)
LiI, NaOAc, DMF (R = Me)	Syn Commun 2 389 (1972)
LiI, NaCN, DMF (R = Me)	Syn Commun 2 389 (1972) JOC 58 100 (1993)
LiI, various pyridines (R = Me, Et)	Rocz 30 323 (1956) Helv 43 113 (1960) Org Syn 45 7 (1965) JCS 6655 (1965)
MgBr ₂ (R = CH ₂ X; X = OMe, SMe, OCH ₂ CH ₂ OMe, OCH ₂ CH ₂ SiMe ₃)	TL 32 3099 (1991)
MgI ₂ (R = 1°, 2°, 3° alkyl; PhCH ₂)	TL 32 5931 (1991)
BCl ₃ (R = Me)	CC 667 (1971)
AlI ₃ (R = Me, Et)	TL 31 3943 (1990)
MeSiCl ₃ , NaI (R = Me, <i>t</i> -Bu, PhCH ₂)	JOC 48 3667 (1983)
Me ₃ SiCl, NaI/H ₂ O (R = 1°, 2°, 3° alkyl; benzylic)	CC 874 (1978) JOC 44 1247 (1979)
Me ₃ SiI (R = 1° alkyl, <i>t</i> -Bu, benzylic)/H ₂ O	Angew Int 15 774 (1976) IACS 99 968 (1977); 106 5335 (1984) CC 495 (1979)
Me ₃ SiSiMe ₃ , I ₂ /H ₂ O (R = Me, Et, PhCH ₂)	Angew Int 18 612 (1979)
PhSiMe ₃ , I ₂ /H ₂ O (R = 1°, 2° alkyl; benzylic)	Syn 417 (1977)
Me ₃ SiOTf, Et ₃ N/H ₂ O (R = <i>t</i> -Bu)	Syn 545 (1980); 1 (1982) (review)
cat <i>t</i> -BuMe ₂ SiOTf (R = <i>t</i> -Bu)	TL 36 711 (1995)
(<i>n</i> -Bu ₃ Sn) ₂ O/H ₃ O ⁺ (R = 1°, 2° alkyl)	Carbohydr Res 162 145 (1987); 177 21 (1988) TL 29 6893 (1988); 32 4239 (1991); 36 3311 (1995) JOC 59 7259 (1994)
CuCl ₂ , glyoxal, H ₂ O (R = Me, Et)	JOC 59 710 (1994)
CuCl ₂ ·2H ₂ O, O ₂ (R = CH ₂ COPh)	TL 36 5401 (1995)
Me ₂ CuLi (R = allyl)	Syn Commun 8 15 (1978) TL 28 5921 (1987)
ZnCl ₂ (R = Et)	Helv 36 1203 (1953)
Hg(OAc) ₂ , CH ₃ OH/KSCN (R = cinnamyl)	TL 2081 (1977)
cat SmCl ₃ , electrolysis (R = allyl)	TL 33 2485 (1992)
O ₃ /Et ₃ N or DBU (R = 3-butenyl)	TL 30 7317 (1989)
NOPF ₆ /H ₂ O (R = benzylic)	Syn 418 (1977)

Ar₃N⁺ (R = benzylic)

Angew Int 21 780 (1982)

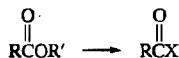
DDQ (R = *p*-MeOC₆H₄CHCH₃)

TL 31 5913 (1990)

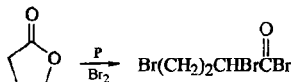


TL 35 7605 (1994)

18. Esters to Acid Halides

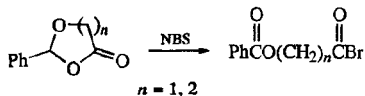


<u>X</u>	<u>R'</u>	<u>Reagent(s)</u>	
F	C(CH ₃)=CH ₂	HF	JOC 34 2486 (1969)
Cl	1° alkyl		Ber 96 1387 (1963)
	C(CH ₃)=CH ₂	HCl	JOC 34 2486 (1969)
	SiMe ₂ (<i>t</i> -Bu)	ClCOCOCI	JOC 43 3972 (1978)
Br	SiMe ₃	Ph ₃ PBr ₂	Syn 684 (1982)
	SiMe ₂ (<i>t</i> -Bu)	Ph ₃ PBr ₂	JOC 51 4941 (1986)
I	1°, 2° alkyl; aryl	I ₂ , H ₂ SiI ₂	JOC 55 3922 (1990)



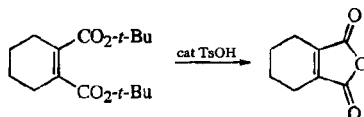
Angew Int 75 1205 (1963)

JOC 52 5745 (1987)



JOC 58 6911 (1993)

19. Esters to Acid Anhydrides

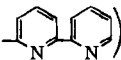


JOC 60 5770 (1995)

20. Esters to Other Esters



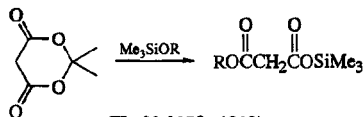
Review: Chem Rev 93 1449 (1993)

NaOMe	Org Syn Coll Vol 2 122 (1943); 5 863 (1973) JOC 56 2122 (1991)
KOR (chiral)	SL 581 (1991)
KOR, NH ₃	JOC 39 855 (1974)
BrMgOR (R ² = CH ₂ SOCH ₃)	JACS 106 2954 (1984)
ROH, <i>n</i> -BuLi (R ¹ = aryl, vinylic)	CC 695 (1986) Org Syn Coll Vol 8 350 (1993)
ROH, K ₂ CO ₃ , cat (<i>n</i> -Bu ₄ N)HSO ₄	TL 29 4567 (1988)
ROH, K ₂ CO ₃ , cat [(<i>n</i> -C ₈ H ₁₇) ₃ NCH ₃]Cl	TL 29 4567 (1988)
<i>t</i> -BuOH, KO- <i>t</i> -Bu, molecular sieves	Syn 49 (1972)
ROH, cat Et ₃ N (R ² = CH=CH ₂)	TL 35 3583 (1994)
ROH, cat DMAP	JOC 50 3618 (1985) (β -keto esters) TL 28 2713, 2717 (1987); 35 3583 (1994) (R ² = CH=CH ₂) JACS 109 7488 (1987)
ROH, cat DMAP, molecular sieves (R = allylic)	JOC 53 449 (1988) (β -keto esters)
ROH, cat KCN	JCS Perkin I 1186 (1972) Syn 790 (1973)
ROH, Δ	JOC 56 1713 (1991)
ROH, molecular sieves (R ² = Me)	Chem Ind 1622 (1966)
ROH (diol), ion exchange resins	JOC 59 1191 (1994) (monoacylation of diol)
ROH (diol), NaHSO ₄ -SiO ₂ or Ce(SO ₄) ₂ -SiO ₂	JACS 111 9102 (1989) JOC 57 312 (1992) (both monoacylation of diol)
ROH, H ₂ SO ₄	Org Syn Coll Vol 3 46 (1955)
ROH, TsOH	Org Syn Coll Vol 3 146 (1955)
ROH, CsF (R ² = )	CL 563 (1980)
BBr ₃ /ROH	TL 3995 (1974)
ROH, Al ₂ O ₃ (R ¹ = Me, R ² = Et; R = 1° > 2° alkyl)	Syn 789 (1981) TL 22 5003, 5007 (1981)
Me ₃ SiI, I ₂ /ROH	Syn 142 (1981)

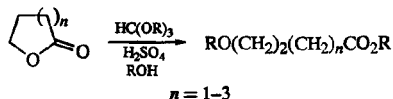
- ROH ($R = 1^\circ, 2^\circ$ alkyl), cat $XSn(n-Bu)_2O-Sn(n-Bu)_2OH$ ($X = Cl, NCS$) TL 27 2383 (1986) ($X = Cl, SCN$)
JACS 110 5198 (1988) ($X = SCN$)
JOC 54 4013 (1989) ($X = SCN$); 56 5307 (1991) ($X = Cl, SCN$); 58 6851 (1993) ($X = SCN$)
- $Me_2Sn(SMe)_2, BF_3 \cdot OEt_2 / RX, CsF$
($R^2 = CHMeCH=CHPh$) TL 30 2959 (1989)
- ROH, $Ti(OR')_4$ ($R' = Et, i-Pr$) Syn 138, 826 (1982)
Helv 65 495 (1982)
Org Syn 65 230 (1987)
JOC 54 4268 (1989); 55 5818 (1990); 56 4875 (1991); 57 3881 (1992)
SL 614, 618 (1991)
Org Syn Coll Vol 8 201 (1993)
- MeOH, cat $(EtO)_3TiOCH_2CH_2OTi(OEt)_3$ ($R = Me$) Helv 65 1197 (1982)
- MeOH, $EtCO_2Me$, cat $Ti(OEt)_4$, $(HOCH_2CH_2OH)$ ($R = Me$) Helv 65 1197 (1982)
- $EtCO_2Me$, cat $Ti(OEt)_4$ ($R = Me$) Helv 65 1197 (1982)
- ROH, electrolysis ($R^2 = p-C_6H_4OH$) TL 22 3715 (1981)
- ROH, catalytic antibody ($R^2 = CH=CH_2$, enantioselective) JOC 57 4756, 6691 (1992)
- ROH, enzyme (enantioselective) Pure Appl Chem 64 1135 (1992) (review)
- ROH, various lipases (enantioselective) TL 30 1703, 7165 (1989); 31 3895, 6663 (1990); 33 3331, 3457, 5389 (1992); 34 2923 (1993); 35 8441 (1994); 36 4185 (1995)
JOC 55 2366 (1990); 58 1287 (1993)
- ROH, porcine pancreatic lipase (enantioselective) Science 224 1249 (1984)
Proc Natl Acad Sci USA 82 3192 (1985)
JACS 107 7072 (1985); 109 3977 (1987); 110 7200 (1988); 112 2849 (1990); 114 8349 (1992)
TL 27 5707 (1986); 28 1607, 2091, 3471 (1987); 29 2455 (1988); 30 6291 (1989); 31 7219 (1990); 32 4197 (1991); 32 5683 (1991); 34 6057 (1993); 35 6047, 8787 (1994)
JOC 53 4939 (1988); 55 3377, 3544, 4187 (1990); 56 1966 (1991); 57 2154, 3231 (1992); 58 1496, 5748 (1993); 59 2891, 7038 (1994)
- ROH, porcine pancreatic lipase, py (enantioselective) JACS 108 5638 (1986)
- ROH, porcine pancreatic lipase, molecular sieves
($R^2 = CH=CH_2$, enantioselective) TL 28 953 (1987); 33 1201 (1992)
- ROH, porcine pancreatic lipase, solid support (enantioselective) TL 28 3563 (1987)
- ROH, porcine pancreatic lipase, ultrasound
($R^2 = CH=CH_2$, enantioselective) TL 36 6069 (1995)

ROH, bovine pancreatic lipase (enantioselective)	TL 34 6057 (1993)
ROH, lipase AK-20 ($R^2 = CH=CH_2$, enantioselective)	TL 35 8743 (1994)
ROH, lipase Amano P (enantioselective)	TL 32 4197 (1991) JOC 58 3980 (1993)
ROH, lipase Amano P-30 ($R^2 = H_2C=CMe$, enantioselective)	JOC 58 7185 (1993); 60 615 (1995)
ROH, lipase Amano PS ($R^2 = CH=CH_2$, enantioselective)	SL 636 (1991); 410 (1992); 289 (1994) JOC 57 1605 (1992); 58 2173, 5717 (1993); 59 388, 7027, 7201, 7214 (1994) TL 34 305 (1993); 36 3715 (1995)
ROH, lipase Amano PS-30 ($R^2 =$ vinylic, enantioselective)	SL 813 (1992) TL 35 5205 (1994); 36 4193 (1995)
ROH, pig liver esterase, solid support (enantioselective)	JACS 106 2687 (1984)
ROH, pig liver esterase-polyethylene glycol monomethyl ether ($R^2 = CH=CH_2$, enantioselective)	TL 36 3833 (1995)
ROH, horse liver esterase, solid support (enantioselective)	TL 28 3563 (1987)
ROH, rabbit liver esterase (enantioselective)	TL 33 5901 (1992)
ROH, α -chymotrypsin (enantioselective)	JACS 108 2767 (1986)
ROH, α -chymotrypsin, solid support (enantioselective)	TL 28 3563 (1987)
ROH, Novo SP-435 ($R^2 = H_2C=CMe$, enantioselective)	SL 813 (1992)
ROH, pancreatin (enantioselective)	JOC 52 5079 (1987)
ROH, Proleather	TL 35 1355 (1994)
ROH, Protease N	TL 35 1355 (1994)
ROH, steapsin (Celite) (enantioselective)	JOC 52 5079 (1987)
ROH, subtilisin (enantioselective)	JACS 108 2767 (1986); 110 584 (1988); 112 945, 2849 (1990); 113 3166 (1991); 114 3901 (1992); 115 12251 (1993) TL 31 3093, 4883 (1990); 35 1353 (1994)
ROH, <i>Aspergillus acylase</i> ($R^2 = CH=CH_2$, enantioselective)	SL 599 (1995)
ROH, <i>Aspergillus melleus</i> (enantioselective)	TL 34 5915 (1993)
ROH, <i>Aspergillus niger</i> (enantioselective)	TL 28 1607 (1987) JACS 109 3977 (1987); 111 386 (1989)
ROH, <i>Candida antarctica</i> (enantioselective)	TL 33 7287 (1992); 34 5793 (1993); 35 6975, 7973 (1994); 36 1675 (1995) JOC 58 653 (1993); 60 3637 (1995)

- ROH, *Candida cylindracea* lipase (enantioselective) JACS 107 7072 (1985); 109 3977 (1987); 112 1164 (1990)
TL 27 29 (1986); 32 5701, 6325, 6865 (1991); 33 5625 (1992); 35 8787 (1994); 36 4349 (1995)
JOC 54 2453, 3161 (1989); 55 4187 (1990); 57 1063 (1992); 59 6018 (1994)
- ROH, *Candida cylindracea* lipase, solid support (enantioselective) JACS 106 2687 (1984)
TL 28 3563 (1987)
- ROH, *Candida rugosa* (enantioselective) JOC 58 3238 (1993)
- ROH, *Chromobacterium* sp. (enantioselective) TL 28 1607 (1987)
- ROH, *Chromobacterium vicosum* (enantioselective) JACS 109 3977 (1987); 112 2849 (1990)
TL 32 6325 (1991)
JOC 60 6057 (1995)
- ROH, *Mucor miehei* (enantioselective) JOC 58 1570 (1993)
TL 36 6545 (1995)
- ROH, *Pseudomonas* lipase ($R^2 = \text{vinyl}$, enantioselective) JACS 110 7200 (1988)
TL 30 1917 (1989); 32 7063 (1991)
- ROH, immobilized *Pseudomonas* ($R^2 = \text{CH}=\text{CH}_2$, enantioselective) TL 31 6403 (1990)
- ROH, *Pseudomonas* AK ($R^2 = \text{CH}=\text{CH}_2$, enantioselective) JOC 55 1138 (1990); 56 2050 (1991); 57 4323 (1992); 58 6483 (1993)
JACS 112 7434 (1990); 113 6129 (1991)
TL 32 4085 (1991)
SL 767 (1993); 1243 (1995)
- ROH, *Pseudomonas* K-10 (enantioselective) JOC 56 2050 (1991); 57 1290 (1992)
SL 491 (1993)
- ROH, *Pseudomonas* sp. ($R^2 = \text{vinyl}$, enantioselective) JOC 53 3127 (1988)
TL 30 1793 (1989); 31 3603, 6797, 7371 (1990); 32 4941, 7021 (1991); 36 6663 (1995)
Syn 948 (1993)
- ROH, *Pseudomonas cepacia* (enantioselective) TL 32 2597, 5159, 5497, 6667, 6671 (1991); 33 3231 (1992); 34 2307, 6581 (1993); 35 7735 (1994); 36 1675, 4865, 6253 (1995)
JACS 114 9414 (1992)
JOC 57 3867, 5643, 6003 (1992); 59 251 (1994)
SL 388 (1992); 339 (1995)
- ROH, *Pseudomonas fluorescens* (enantioselective) TL 29 5173 (1988); 30 6189 (1989); 31 1601, 5657 (1990); 34 3785, 4205, 4439 (1993)
JOC 53 6130 (1988); 54 2646 (1989); 55 4187, 4237, 6214 (1990); 58 5000 (1993); 59 1751, 2891 (1994)
SL 545 (1990); 310 (1991); 108 (1993); 754 (1994)
Tetr Asym 2 733 (1991) (review)
- ROH, *Pseudomonas fragi* ($R^2 = \text{CH}=\text{CH}_2$, enantioselective) TL 30 6189 (1989)



TL 30 3073 (1989)



JOC 59 2253 (1994)



R²OH, lipase

TL 34 1367 (1993)

$$\text{R}^2\text{OH, cat } n\text{-Bu}_3\text{P (R}^1 = 2\text{-pyridyl)}$$

JOC 58 7286 (1993)

$$\text{R}^2\text{OH}, \text{AgO}_2\text{CCF}_3 \text{ (R}^1 = t\text{-Bu)}$$

TL 24 5143 (1983)

JCS Perkin I 121, 131 (1987)

Org Syn Coll Vol 8 71 (1993)

$$R^2OH, Hg(O_2CCF_3)_2$$

JACS 97 3515 (1975)

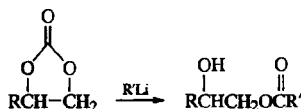
Org Syn Coll Vol 7 87 (1990)

$$R^2OH, HgCl_2 (CdCO_3) \text{ or } Tl(O_2CCF_3)_3$$

JACS 97 3515 (1975)

$$\text{R}^2_2\text{CuLi}, \text{O}_2 \text{ (R}^1 = 2\text{-pyridyl)}$$

CC 1231 (1981)



R' = alkyl, aryl, alkynyl, vinylic

JACS 117 2409 (1995)

21. Esters to Amides

 NH_3

Org Syn Coll Vol 1 153, 179 (1941); 3 516, 536 (1955)

JOC 52 4379 (1987); 56 146, 151 (1991); 59 2179

(1994) (lactone)

TL 32 5359 (1991) (R = vinylic)

JACS 117 2479 (1995)

 $\text{NH}_3, \text{NH}_4\text{X}$

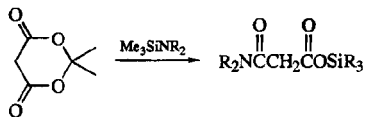
JACS 60 579 (1938)

NH₃, immobilized *Candida antarctica* lipase
(R' = vinylic, alkynyl)

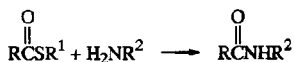
SL 529 (1994)

NH ₃ or R ₂ NH, <i>Candida antarctica</i> (enantioselective)	Tetr Asym 3 1519 (1992) TL 34 6141 (1993) (β -keto esters); 36 4349 (1995) Tetr 49 4007 (1993)
RNH ₂	JOC 56 1713 (1991) (R = <i>t</i> -Bu); 57 5868 (1992); 58 735, 6596 (1993); 59 2092 (1994) (lactone) TL 32 5359 (1991) (R = vinylic); 35 3583 (1994) (R = CH=CH ₂)
RNH ₂ (CF ₃ CO ₂ Et)	TL 33 397 (1992); 36 3451, 7357 (1995) CC 2613 (1994)
<i>n</i> -BuNH ₂ , C ₆ H ₆ (R' = aryl > alkyl)	TL 27 2263 (1986)
RNH ₂ , cat KCN	TL 32 5359 (1991) (R = vinylic)
RNH ₂ , lipase SP 382	TL 32 761 (1991)
R ₂ NH	JACS 71 2215 (1949) Org Syn Coll Vol 3 108, 765 (1955); 4 80 (1963) JOC 22 1225 (1957) (lactone); 56 1713 (1991); 58 735 (1993) TL 35 931 (1994) (lactone)
R ₂ NH, 2-hydroxypyridine	JCS C 89 (1969) JOC 51 4836 (1986)
R ₂ NH, NaOCH ₃	JOC 28 2915 (1963)
R ₂ NH, cat NaCN	JOC 52 2033 (1987)
R ₂ NH, electrolysis	TL 28 441 (1987)
R ₂ NH, various enzymes (enantioselective)	TL 28 1629 (1987)
R ₂ NH, chymotrypsin (enantioselective)	TL 30 2787 (1989)
R ₂ NH, porcine pancreatic lipase (enantioselective)	Proc Natl Acad Sci USA 82 3192 (1985)
R ₂ NH, subtilisin Carlsberg or subtilisin BPN' (enantioselective)	JACS 111 386 (1989)
R ₂ NH, subtilisin 8350 (enantioselective)	JACS 112 945 (1990)
R ₂ NH, <i>Aspergillus</i> acylase (R = CH=CH ₂ , enantioselective)	SL 599 (1995)
R ₂ NH, <i>Candida cylindracea</i> (enantioselective)	TL 29 6973 (1988); 30 5345 (1989) Tetr 49 4007 (1993)
R ₂ NH, <i>Pseudomonas</i> PS (enantioselective)	TL 36 5155 (1995)
NH ₄ OH, NH ₄ Cl	Org Syn Coll Vol 4 486 (1963)
LiNR ₂	TL 1791 (1970); 33 6453 (1992); 36 4555 (1995) JOC 52 5745 (1987); 53 5130 (1988) (lactones)
NaNH ₂ , NH ₃	JOC 56 4499 (1991)
NaNR ₂	JACS 77 469 (1955) TL 321 (1971) Chem Ind 277 (1956)
KNHR (chiral)	SL 581 (1991)

MgNR_2	JCS 1188 (1954)
$\text{Me}(\text{MeO})\text{NH}\cdot\text{HCl}$, <i>i</i> -PrMgCl	TL 36 5461 (1995)
$\text{BBr}_3/\text{R}_2\text{NH}$	TL 3995 (1974)
R_2NH , AlCl_3	Syn 306 (1991)
RNH_2 or R_2NH , Et_2AlCl	TL 35 7605 (1994) (β -lactone)
Me_2AlNH_2	JOC 53 5315 (1988)
Me_3Al , NH_4Cl or $(\text{RNH}_3)\text{Cl}$ or $(\text{R}_2\text{NH})\text{Cl}$	Syn Commun 12 989 (1982) JOC 54 1787 (1989); 55 6352 (1990); 57 1262 (1992); 59 1231 (1994) JACS 114 9309 (1992); 115 11434 (1993)
Me_3Al , RNH_2 or R_2NH	TL 4171 (1977); 36 1813 (1995) Org Syn 59 49 (1980) JACS 107 1695, 5732 (1985) JOC 52 4665 (1987); 56 2883 (1991); 58 6229 (1993); 60 4542 (1995) Org Syn Coll Vol 6 492 (1988) SL 1007 (1992)
MeAlClNHAr	JOC 54 3321 (1989) (lactones)
$\text{R}_2\text{AlCl}\cdot\text{HNMe}_2$ ($\text{R} = \text{Me}$, <i>i</i> -Bu)	JOC 59 1231 (1994)
$\text{LiAl}(\text{NHR})_4$	JOC 57 5831 (1992)
$\text{NaEt}_2\text{Al}(\text{NR}_2)_2$	SL 827 (1994)
Me_3SiNR_2	TL 35 7605 (1994) (β -lactone)
$\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, RNH_2 or R_2NH	JOC 57 6101 (1992)
$\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, $(\text{R}_2\text{NH}_2)\text{Cl}$	SL 850 (1993)
R_3SnNR_2	JCS A 992 (1969) JCS C 2565 (1969) Syn 319 (1983) (lactones)
$\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$, $\text{Me}_2\text{NCH}_2\text{CH}_2\text{OH}/\text{RNH}_2$	TL 34 7217 (1993)
$\text{Ti}(\text{NR}_2)_4$	JCS C 2565 (1969)
NBS , cat $(\text{PhCO}_2)_2/\text{R}_2\text{NH}$	SL 219 (1994)
KOH , $n\text{-Bu}_4\text{NBr}/\text{R}_2\text{NH}$, $(o\text{-NO}_2\text{C}_6\text{H}_4\text{O})_2\text{POPh}$, molecular sieves	CL 285 (1981)



TL 30 3073 (1989)



CuI

JOC 52 4531 (1987)



TL 28 3019 (1987); 35 2067 (1994)

Tetr 48 1145 (1992)



CL 915 (1986); 293 (1987) (both intramolecular)

22. Esters to Nitriles



TL 4907 (1979)

JOC 52 1309 (1987); 57 2888 (1992)

23. Amides to Carboxylic Acids

acidic resin, H₂O

Chem Ind 736 (1957)

JOC 46 5351 (1981)

HCl, H₂O

Org Syn Coll Vol 3 66, 88 (1955); 4 39, 496 (1963)

JOC 59 1904 (1994)

HCl, HOAc, H₂O

JACS 63 2494 (1941)

HBr, PhOH

JOC 59 1904 (1994)

H₂SO₄, H₂O

JACS 70 3091 (1948); 113 7388 (1991)

H₃PO₄, H₂O

Rec Trav Chim 46 600 (1927)

NaOH

Org Syn Coll Vol 4 58 (1963)

NaOH, ethylene glycol

JACS 78 450 (1956); 79 2530 (1957)

KOH

JOC 52 4689 (1987); 58 898 (1993)

KOH, ethylene glycol

TL 27 4941 (1986)

KOH, diethylene glycol

JOC 15 617 (1950)

KO-*t*-Bu, H₂O, Et₂O

JACS 98 1275 (1976)

TL 32 1275 (1991)

Na₂O₂, H₂O

JOC 40 1187 (1975); 59 4853 (1994)

N₂O₄ (RCONHR')

JACS 111 4522 (1989); 115 5843 (1993)

TL 31 3893 (1990)

N₂O₄, HOAc (RCONHR')

JACS 60 235 (1938)

N₂O₄, NaOAc/H₂, cat Pd(OH)₂-C (RCONHR')

JOC 56 3744 (1991)

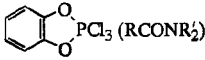
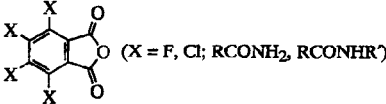
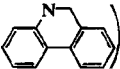
NOCl, Ac₂O, HOAc, py / KOH (RCONHR')

JACS 83 1492 (1961)

(NO)BF₄, CH₃CN (RCONHR')


JOC 30 2386 (1965)

TL 27 4941 (1986)

<i>n</i> -BuONO, HCl, HOAc (RCONHR')	JACS 70 3091 (1948) J Med Chem 9 603 (1966)
NaNO ₂ , H ₂ SO ₄ (RCONH ₂)	JACS 78 5416 (1956); 79 2530 (1957); 107 2111 (1985) JOC 60 7739 (1995)
HOSO ₂ ONO, H ₂ O (RCONH ₂)	Org Prep Proc Int 14 357 (1982)
 (RCONR' ₂)	Ber 96 1387 (1963)
AcOCH ₂ CM ₂ COCl/LiOH (RCONHR')	TL 31 731 (1990)
 (X = F, Cl; RCONH ₂ , RCONHR')	TL 29 6553 (1988)
glyoxal, CuCl ₂ , H ₂ O (RCONH ₂ , RCONHR')	JOC 59 710 (1994)
CAN (NR ₂ = )	CL 1551 (1981)
acylase I (enantioselective)	JACS 111 6354 (1989) JOC 58 954 (1993); 60 2292 (1995)
penicillin acylase (enantioselective)	SL 339 (1993); 65 (1994)
porcine kidney acylase I (enantioselective)	JOC 54 4511 (1989)
<i>Mycobacterium neoaurum</i> (enantioselective)	JOC 53 1826 (1988)
<i>Pseudomonas putida</i> aminopeptidase (enantioselective)	JOC 57 6769 (1992)

24. Amides to Esters



MeOH, acidic resin	JOC 46 5351 (1981)
MeOH, TsOH	JOC 57 4037 (1992)
MeOH, BF ₃ ·OEt ₂	CC 414 (1969)
EtOH, HCl	Arch Pharm 290 218 (1957) JOC 25 560 (1960); 35 125 (1970)
R''OH, SOCl ₂ , LiI (R = H)	SL 489 (1993)
R''OH, DBU (NR ₂ = N )	JOC 50 3224 (1985)
(<i>t</i> -BuO ₂ C) ₂ O, cat DMAP/NaOR'' (R' = H)	JOC 56 5482 (1991)
(Me ₃ O)BF ₄ /HCO ₂ H, H ₂ O (R'' = Me)	JACS 111 3382 (1989)

R''Br, H₂O

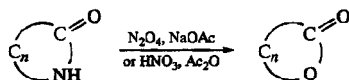
JOC 34 3204 (1969); 58 1804 (1993)

N₂O₄, NaOAc, HOAc/Δ (on RCONHR'')JACS 76 4497 (1954); 77 6008, 6011 (1955)
TL 2627 (1965)

JOC 34 3834 (1969)

NaNO₂, Ac₂O, HOAc/Δ (on RCONHR'')

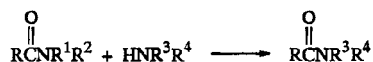
JACS 77 6008, 6011 (1955)



Tetr 45 863 (1989)

25. Amides to Other Amides

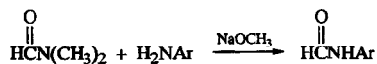
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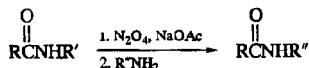
Reagent

Amide Conversion

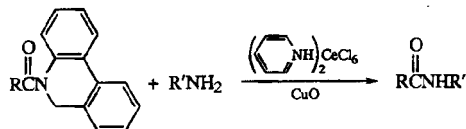
Δ	DMF → 2°, 3°	Syn 361 (1973)
NaH	DMF → 2°	JOC 26 2563 (1961)
NaNH ₂	DMF → 2°	JOC 26 2563 (1961)
NaOMe	DMF → 2°	JOC 24 895 (1959); 26 2563 (1961)
HCl	1° → 2°	JACS 65 1566 (1943)
H ₂ SO ₄	DMF → 2°	Syn 361 (1973)
HNO ₃ , Ac ₂ O	2° → 1°, 2°, 3°	JOC 49 3322 (1984)
HOAc	HCONH ₂ → HCONR ^{Ar} (R = H or alkyl)	JCS 67 830 (1895)
BF ₃	1° → 2°, 3°	JACS 59 1202 (1937)
AlCl ₃	1° → 2°, 2° → 2°, 3°	JOC 59 4035 (1994)
Me ₃ SiCl	DMF → 3°	SL 659 (1992)
Cu(NO ₃) ₂ ·3H ₂ O, Ac ₂ O	2° → 1°, 2°, 3°	JOC 49 3322 (1984)
(NO ₂)BF ₄ , py	2° → 1°, 2°, 3°	JOC 49 3322 (1984)
N ₂ O ₅ , Ac ₂ O	2° → 1°, 2°, 3°	JOC 49 3322 (1984)
N ₂ O ₄ , NaOAc	2° → 1°, 2°, 3° 2° → 2°	JOC 49 3322 (1984) TL 23 1127 (1982)
CO ₂	DMF → 2°, 3°	BCSJ 41 1485 (1968)
(<i>t</i> -BuO ₂ C) ₂ O, DMAP	1° → 2°, 3° 2° → 2°, 3°	JOC 56 5482 (1991) CC 1317 (1985)



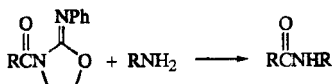
JOC 26 2563 (1961)



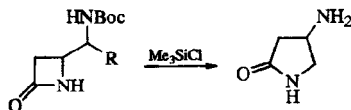
TL 23 1127 (1982)



CL 991 (1982)



BSCF II 167 (1982)



TL 33 4827 (1992)

 $\text{R}^2\text{CO}_2\text{H}$, cat H^+

JCS C 1337 (1967)

 $\text{R}^2\text{CO}_2\text{H}$, AlCl_3

JCS C 1337 (1967)

JCS Perkin II 300 (1972)

 $(\text{R}^2\text{CO})_2\text{O}$, H^+ or AlCl_3

JCS C 1337 (1967)

 $(\text{CF}_3\text{CO})_2\text{O}$ / DBN

JCS Perkin I 1629 (1979)

 R^2COCl , zeolite

TL 35 8877 (1994)

base, RBr (intramolecular, β -lactam)

See page 1861, Section 8.

Na, Me_2SO_4 (R = Me)

Ber 68 751 (1935)

Na, RX (R = 1° alkyl, PhCH_2 ; X = Cl, Br, I)

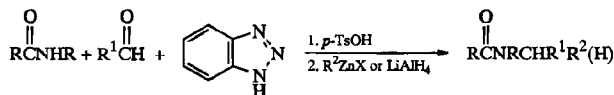
Ber 10 327 (1877)

JACS 74 1010 (1952)

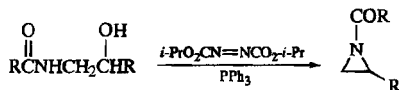
NaH/ Me_2SO_4 (R = Me)

JOC 57 4767 (1992)

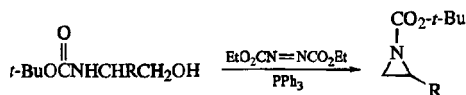
NaH, RX (R = 1°, 2° alkyl; allylic; benzylic; X = Br, I)	JOC 14 1099 (1949); 57 4802 (1992); 59 4194 (1994) JACS 74 1010 (1952); 110 8153 (1988)
NaH, ArX-Cr(CO) ₃ (X = F, Cl)	TL 33 4049 (1992)
NaH, ArPh(OAc) ₃	TL 33 6875 (1992)
KH, RX (RX = 1° alkyl Cl or Br or I, benzylic Cl or Br)	JOC 53 3164 (1988) TL 32 2441 (1991)
NaOH, K ₂ CO ₃ , C ₆ H ₆ , cat (n-Bu ₄ N)HSO ₄ , RX (R = 1° alkyl, benzylic; X = Cl, Br)	Syn 527, 549 (1979); 1005 (1981)
NaOH, (Et ₃ NCH ₂ Ph)Cl, aq C ₆ H ₆ , RX [RX = Me ₂ SO ₄ , Et ₂ SO ₄ ; 1° alkyl and benzylic Cl, Br, I; R ² = aryl]	Syn 113 (1976)
KOH, acetone, MeI (R ² = Ar; R = Me)	JACS 74 1321 (1952)
KOH, EtI (R = Et)	Ber 20 3422 (1887)
KOH, EtOH, RBr (R = 1° alkyl)	JACS 74 1010 (1952)
KOH, DMSO, RX (R = 1°, 2° alkyl, PhCH ₂ ; X = Cl, Br, I)	Syn 266 (1971) Tetr 35 2169 (1979)
KO- <i>t</i> -Bu, crown ether / RX (RX = MeI, allyl bromide; R ² = aryl)	Syn Commun 9 757 (1979)
K ₂ CO ₃ , Me ₂ SO ₄ or BrCH ₂ CO ₂ Et	JOC 57 4767 (1992)
K ₂ CO ₃ , cat (PhCH ₂ NEt ₃)Cl, RCHBrCO ₂ R (R ¹ = CX ₃)	JOC 56 420 (1991) (X = F); 57 1603 (1992) (X = Cl)
K ₂ CO ₃ , Cu, ArBr	TL 36 133 (1995)
K ₂ CO ₃ , CuI, ArBr(I)	TL 36 8809 (1995)
<i>n</i> -BuLi / Me ₂ SO ₄ (R = Me)	JOC 38 1677 (1973)
KF, alumina, RX (RX = MeI, PhCH ₂ Cl)	CL 1143 (1981)
ROH, EtO ₂ CN=NCN ₂ Et, PPh ₃ (intramolecular, β-lactam)	See page 1861, Section 8.
ROH, Me ₂ NCON=NCNMe ₂ , <i>n</i> -Bu ₃ P (R = 1° alkyl, 1° benzylic, 1° allylic; R' = CF ₃)	TL 35 5081 (1994) CL 539 (1994)
ROH, <i>n</i> -Bu ₃ P=CHCN (R = 1° alkyl, 1° benzylic, 1° allylic; R' = CF ₃)	TL 35 5081 (1994)
R'CHO or R' ₂ CO, H ₂ , cat Pd-C, Na ₂ SO ₄ (R = CH ₂ R' or CHR' ₂)	TL 35 3313 (1994)
R' ₂ C(OR'') ₂ (R'' = Me, Et), H ₂ , cat Pd-C, HOAc, H ₂ SO ₄ (R ² = H, R = CHR' ₂)	JOC 27 2205 (1962)

R² = benzylic, aryl, alkynyl

JOC 58 2086 (1993)



TL 33 6267 (1992)

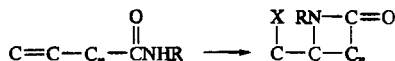


TL 34 6513 (1993)

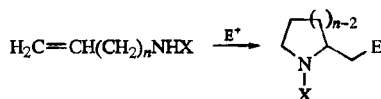


R = 1° or 2° alkyl, 1° benzylic, 1° or 2° allylic, 2° propargylic

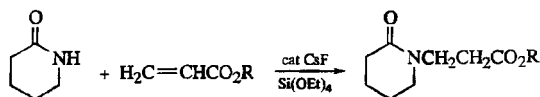
TL 36 8681 (1995)



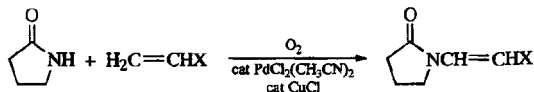
See page 1861, Section 8.

X = COR, CO₂R, SO₂Ar

See page 761, Section 3.



TL 35 1875 (1994)

X = CHO, COR, CO₂R, CONR₂

TL 33 6643 (1992)



R'

2° alkyl, PhCH₂PhCH₂

Reagent(s)

Li or Na, ultrasound

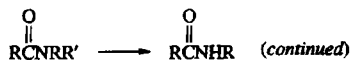
Li, NH₃/H₂O

HBr

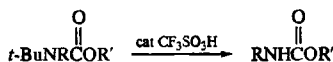
TL 31 941 (1990)

JOC 46 5383 (1981)

JOC 41 3853 (1976)

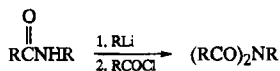


<u>R'</u>	<u>Reagent(s)</u>	
	O ₂ , KO- <i>t</i> -Bu, DMSO	SL 561 (1992)
	PhOH, orthophosphoric acid	JOC 41 3853 (1976)
<i>p</i> -MeOC ₆ H ₄ CH ₂	CAN	CL 1001 (1983)
		TL 29 1409 (1988); 36 729 (1995)
		JACS 113 6621 (1991)
	<i>t</i> -BuLi/O ₂ or MoO ₅ ·py·HMPA	TL 30 451 (1989)
<i>o</i> -NO ₂ C ₆ H ₄ CH ₂	hν	JOC 58 4599 (1993)
PhCHCH ₃	Li, NH ₃ , H ₂ O	TL 27 4941 (1986)
		JOC 51 5226 (1986)
	Na, NH ₃	TL 29 151 (1988); 30 5239 (1989)
		JOC 56 4868 (1991)
		JACS 117 5169 (1995)
	HCO ₂ H	JACS 102 7505 (1980)
PhCHCH ₂ OH	Li, NH ₃ , EtOH	JOC 57 1656 (1992); 58 36 (1993)
	K, NH ₃ , EtOH	JOC 58 36 (1993)
<i>p</i> -MeOC ₆ H ₄ CHCH ₃	CAN, SiO ₂	JOC 53 4773 (1988)
<i>p</i> -MeOC ₆ H ₄	electrolysis	TL 29 1497 (1988)
	CAN	JOC 47 2765 (1982); 53 3784 (1988);
		57 4155 (1992); 58 1646 (1993)
		TL 28 3593 (1987); 29 2779 (1988);
		33 5737 (1992)
	(NH ₄) ₂ S ₂ O ₈ , cat AgNO ₃	JACS 109 1129 (1987)
		SL 229 (1990)

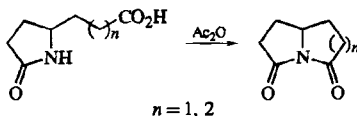


SL 621 (1990)

26. Amides to imides



JOC 54 228 (1989); 56 1822 (1991)



See page 1949, Section 5.

27. Amides to Nitriles



Review: Chem Rev 42 189 (1948)

SOCl_2	Ann 274 312 (1893) Helv 26 1125 (1943) JACS 69 2663 (1947); 78 494 (1956); 82 2498 (1960) JOC 27 4608 (1962) Org Syn Coll Vol 4 436 (1963)
SOCl_2 , DMF	JACS 80 6600 (1958); 88 2025 (1966) JOC 24 26 (1959); 36 3960 (1971); 50 2323 (1985); 55 2155 (1990) Tetr 19 161 (1963); 21 2239 (1965) Chem Ind 752 (1964) JOC USSR 11 652 (1975)
SOCl_2 , py	JOC 53 5315 (1988)
HOSO_2NH_2	J Gen Chem USSR 20 303 (1950)
ClSO_2NCO , Et_3N	CC 227 (1979)
PhSO_2Cl	JCS 763 (1946)
PhSO_2Cl , py	JACS 77 1701 (1955)
TsCl , py	JACS 77 1701 (1955) BSCF 2262 (1965)
	JOC USSR 12 1563 (1976)
	TL 27 1925 (1986)
$\text{MeO}_2\text{C}\bar{\text{N}}\text{SO}_2^+\text{NEt}_3$	TL 29 2155 (1988)
P_2O_5	JACS 83 2354, 2363 (1961); 114 9309 (1992) JOC 27 4608 (1962) Org Syn Coll Vol 4 144, 486 (1963)
P_2O_5 , $\text{Me}_3\text{SiOSiMe}_3$	Syn 591 (1982) JOC 54 4939 (1989)
$(\text{Ph}_3\text{PO}_3\text{SCF}_3)_3\text{O}_3\text{SCF}_3$	TL 277 (1975)
polyphosphate ester	Chem Pharm Bull 18 397 (1970)
$(\text{EtO})_2\text{POP}(\text{OEt})_2$	JACS 88 2025 (1966)
$(\text{EtO})_3\text{PI}_2$	TL 1725 (1979)
	JACS 88 2025 (1966)

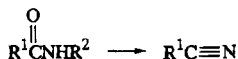
DCC, py

JOC 26 3356 (1961); 36 3960 (1971)

JACS 88 2025 (1966)

LiAlH₄

Can J Chem 44 2113 (1966)

R¹R²Reagent

aryl

benzylic

cat ClRh(PPh₃)₃

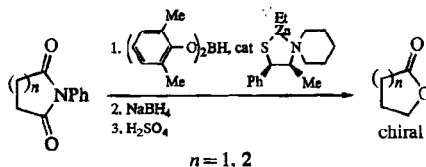
TL 1963 (1970)

alkyl, aryl, vinylic

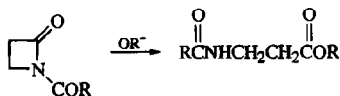
n-BuPOCl₃Org Prep Proc Int 15
297 (1983)

28. Imides to Esters or Lactones

See also page 1990, Section 34.



TL 36 4265 (1995)

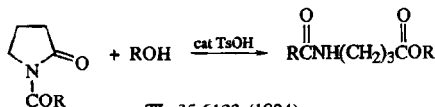


JOC 56 1681 (1991); 59 515, 6156 (1994)

J Med Chem 35 4230 (1992)

Tetr 48 6985 (1992)

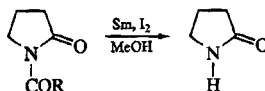
TL 35 5543 (1994)



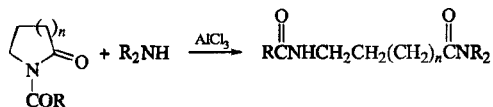
TL 35 6133 (1994)

29. Imides to Amides

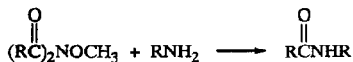
See also page 1985, Section 28, and page 1990, Section 34.



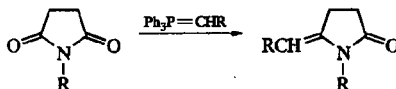
SL 1261 (1995)

 $n = 1-3$

SL 747 (1992)

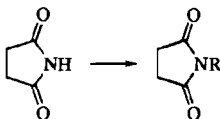


TL 31 243 (1990)



Syn 685 (1975) (review)

JCS Perkin I 2567 (1993)

30. Imides to Other Imides $\text{R}_2\text{CHOMs, CsF}$

SL 336 (1995)

 NaH/ArPb(OAc)_3

TL 33 6875 (1992)

 $\text{ROH, R'O}_2\text{CN=NCO}_2\text{R', PPh}_3$

JACS 94 679 (1972)

JOC 52 5127 (1987); 60 5352 (1995)

TL 35 665 (1994)

See also page 779, Section 4.

31. Nitriles to Carboxylic Acids $\text{HCl, H}_2\text{O}$

Org Syn Coll Vol 1 21, 289, 336, 451 (1941); 3 84,
114, 591, 851 (1955); 4 496, 804 (1963)
JOC 53 5552 (1988); 58 898 (1993)
TL 31 1249 (1990); 32 2605 (1991)

 $\text{HCl, H}_2\text{O, HOAc}$

Org Syn Coll Vol 4 790 (1963)

 $\text{HBr, H}_2\text{O}$

Org Syn Coll Vol 1 131 (1941)

 $\text{H}_2\text{SO}_4, \text{H}_2\text{O}$

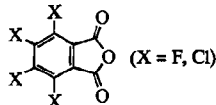
Org Syn Coll Vol 1 406, 436 (1941); 2 25, 588
(1943); 3 557 (1955)

H_3PO_4

Rec Trav Chim 46 600 (1927)

 $\text{CF}_3\text{CO}_2\text{H}$, cat $\text{Hg}(\text{O}_2\text{CCF}_3)_2/\text{N}_2\text{O}_4$

JOC 54 2539 (1989)



TL 29 6557 (1988)

 NaOH , $\text{H}_2\text{O}/\text{H}^+$

Org Syn Coll Vol 1 321 (1941); 2 376 (1943)

 NaOH , H_2O , MeOH/H^+

JACS 107 7967 (1985)

 NaOH , H_2O , EtOH/H^+

JOC 56 3102 (1991)

 NaOH , ethylene glycol/ H^+

JACS 78 450 (1956)

JOC 51 4169 (1986)

 NaOH , diethylene glycol/ H^+

JOC 50 2128 (1985)

 NaOH , H_2O_2

JOC 60 6148 (1995)

 KOH , H_2O , EtOH/H^+

Org Syn Coll Vol 2 292 (1943)

JOC 57 441 (1992)

 KOH , ethylene glycol/ H^+

JACS 78 5413 (1956)

Org Syn Coll Vol 4 93 (1963)

 $\text{Ba}(\text{OH})_2$, $\text{H}_2\text{O}/\text{H}^+$

Org Syn Coll Vol 1 298 (1941); 3 34 (1955)

bacteria

Apl Environ Microbiol 31 900 (1976)

Biochem J 165 309 (1977)

Adv Biochem Engin 12 1 (1980)

Agric Biol Chem 46 1165 (1982)

J Biochem 117 677 (1985)

J Gen Microbiol 132 1493 (1986)

TL 28 4057 (1987); 29 2589 (1988)

nitrilase *Rhodococcus butanica* (enantioselective)

TL 32 1343 (1991)

nitrilase *Rhodococcus* sp. (enantioselective)

TL 31 7223 (1990); 32 341 (1991)

JOC 58 3179 (1993)

32. Nitriles to Esters

 $\text{R}'\text{OH}$, HCl

Ber 105 1778 (1972)

JOC 50 2128 (1985)

TL 27 2103 (1986)

JOC 51 5463 (1986)

SL 45 (1992)

 $\text{R}'\text{OH}$, HCl , silica gel

JOC 59 3769 (1994)

 $\text{R}'\text{OH}$, H_2SO_4

JOC 50 2128 (1985); 53 4063 (1988)

 $\text{R}'\text{OH}$, H_2SO_4 , H_2O

Org Syn Coll Vol 1 270 (1941)

 $\text{R}'\text{OH}$, TsOH

JOC 23 1225 (1958)

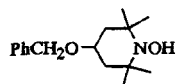
 NaOH/MeI ($\text{R}' = \text{Me}$)

JACS 108 1039 (1986)

33. Nitriles to Amides



H ₂ O, cat RuH ₂ (PPh ₃) ₄	JOC 57 2521 (1992)
H ₂ O, cat PtH(Me ₂ POHPOMe ₂)(Me ₂ POH)	TL 36 8657 (1995)
H ₂ O, cat Cu	JOC 47 4812 (1982)
H ₂ SO ₄	JACS 78 5416 (1956); 79 2530 (1957)
CF ₃ SO ₃ H, Al ₂ O ₃	TL 36 3469 (1995)
PPA	JACS 76 3039 (1954); 79 725 (1957)
HCl	JOC 57 7235 (1992)
HCl, H ₂ O	Org Syn Coll Vol 3 66, 88 (1955); 4 58, 496, 760 (1963)
BF ₃ , HOAc	JOC 20 1448 (1955) JACS 79 725 (1957)
BF ₃ , HOAc, H ₂ O	JOC 20 1448 (1955)
Al ₂ O ₃	TL 36 3469 (1995)
Al ₂ O ₃ , KF	Syn Commun 12 177 (1982)
TiCl ₄ , HOAc	CL 357 (1973)
Hg(OAc) ₂ , HOAc	JOC 54 718 (1989)
NaO ₂ , DMSO	JOC 44 4727 (1979)
H ₂ O ₂ , base	Ber 17 1289 (1884); 18 355 (1885) JACS 39 103 (1917); 56 2749 (1934); 75 3961 (1953); 77 2519 (1955); 110 497 (1988) Org Syn Coll Vol 2 44, 586 (1943) JOC 36 3048 (1971); 57 4441 (1992); 58 898 (1993); 59 3769 (1994) BCSJ 54 793 (1981)
H ₂ O ₂ , K ₂ CO ₃ , DMSO	Syn 949 (1989)
H ₂ O ₂ , cat K ₂ CO ₃ , urea	Syn Commun 23 3149 (1993)
H ₂ O ₂ , NH ₄ OH	JOC 51 1065 (1986)
H ₂ O ₂ , NaOH, (n-Bu ₄ N)HSO ₄ (phase transfer)	Syn 243 (1980)
Na ₂ CO ₃ ·3/2H ₂ O ₂ , H ₂ O, acetone (R = Ar)	Syn Commun 20 1445 (1990)
NaBO ₃ ·4H ₂ O, H ₂ O (R = Ar)	Tetr 45 3299 (1989) Syn Commun 20 563 (1990)
K(Na)B(OH) ₄ or borax, H ₂ O (α-hydroxynitriles)	TL 30 563 (1989)
KOH, diethylene glycol	JOC 15 617 (1950)
KOH, t-BuOH	JOC 41 3769 (1976)



Syn 1034 (1984)

MnBr(CO)₅, NaOH, (PhCH₂NEt₃)Cl

J Chem Res (S) 456 (1986)

MnO₂-SiO₂

Syn 715 (1988)

TL 35 1401 (1994)

RuCl₃(NH₃)₅, Ag₂O, CF₃CO₂H/Zn/Ag₂O,
CF₃CO₂H/Zn

TL 4025 (1974)

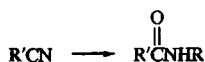
nitrilase *Rhodococcus butanica* (enantioselective)

TL 32 1343 (1991)

nitrilase *Rhodococcus* sp. (enantioselective)

TL 32 341 (1991)

JOC 58 3179 (1993)

RX (R = 1°, 2°, 3° alkyl, benzylic; X = F, Cl, Br, I), Syn 274 (1979)
NOPF₆

RBr, AgOTf (R = 3° alkyl)

JOC 53 5315 (1988)

R₇CH₂CH₂I, electrolysis

JOC 53 5714 (1988)

KOH, *t*-BuOH/1° RBr(I)

Syn 303 (1978)

ROH, H⁺

Org Rxs 17 213 (1969) (review)

"Comprehensive Organic Synthesis," Eds. B.M.
Trost and I. Fleming, Pergamon, Oxford (1991),
Vol 6, Part 1.9, p 261 (review)ROH, H₂SO₄

Org Syn Coll Vol 5 73 (1973)

ROH, CF₃SO₃H

TL 32 4317 (1991)

ROH, (CF₃SO₂)₂O/NaHCO₃

TL 30 581 (1989)

RNH₂, H₂O, cat H₂Ru(PPh₃)₄

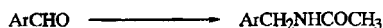
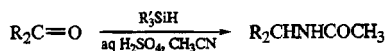
JACS 108 7846 (1986)

(H₂CO)_m, ArH, H⁺ (R = CH₂Ar)

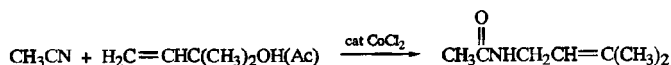
JACS 115 1321 (1993)

R''CHO, Cl₃SiH, H₂O (R = CH₂R'')

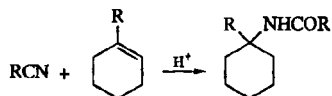
TL 32 1825 (1991)



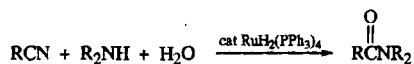
JOC 39 2740 (1974)



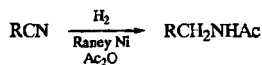
JOC 60 2670 (1995)



For this and related reactions, see page 1628, Section 3.

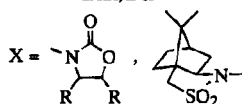
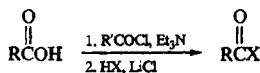


JACS 108 7846 (1986)

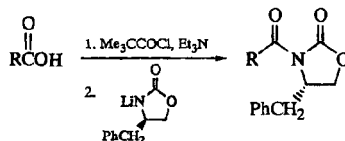


See page 1957, Section 15.

34. Other Interconversions

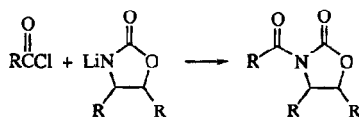


JOC 60 2271 (1995)



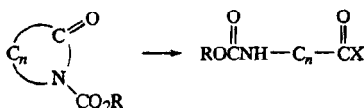
JACS 111 1063 (1989)

JOC 60 6198, 7153 (1995)

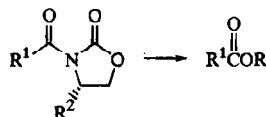



Org Syn Coll Vol 8 339 (1993)

JACS 112 5290 (1995)



<u>X</u>	<u>n</u>	<u>Reagent(s)</u>	
OH	5	LiOH	SL 63 (1990)
OR	2	NaOR	TL 34 4149 (1993)
			JOC 59 515 (1994)
		NaOR	SL 561 (1992)
NHR	4	NaOR	SL 63 (1990)
	5	NaOR	
	2	RNH ₂	JOC 59 1249 (1994)
NR ₂	3, 4	RNH ₂ , pressure	TL 33 4945 (1992)
	4	R ₂ NH, AlCl ₃	SL 747 (1992)
	5	LiNR ₂	SL 63 (1990)

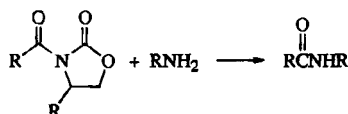


ROH, MeMgBr or MgBr₂, 

TL 34 5563 (1993) (enantioselective)

LiOR

SL 155 (1993)

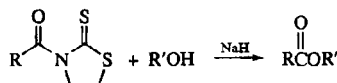


Me₃Al

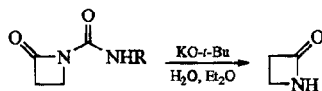
JACS 114 9434 (1992)

cat Cp₂MCl₂ (M = Ti, Zr)

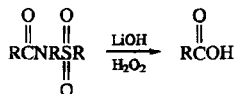
JOC 59 3506 (1994)



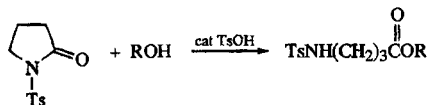
JOC 57 1591 (1992)



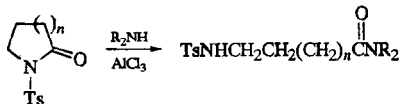
JOC 57 3490 (1992)



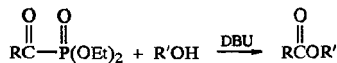
TL 30 5603 (1989)



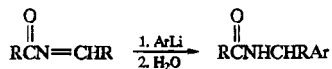
TL 35 6133 (1994)


 $n = 1-3, 9$

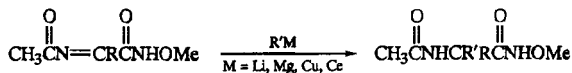
JOC 59 1904 (1994)



TL 22 3617 (1981)



TL 36 8003 (1995)



TL 27 4241 (1986)



ROH

JACS 110 7910 (1988)

ROH, cat *n*-Bu₃P

JOC 58 7286 (1993)

CatalystClRh(PPh₃)₃

JACS 89 2338 (1967)

Pd(PPh₃)₄

JOC 51 898 (1986)

NaBH₄, NiCl₂·6H₂O

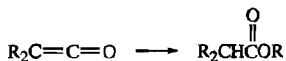
Syn Commun 22 1339 (1992)

Zn(BH₄)₂

JOC 59 4114 (1994)

(PhCH₂NEt₃)₂MoS₄

JOC 60 7682 (1995)

ROH, R₃N

TL 26 381 (1985)

ROH, cat *n*-Bu₃P

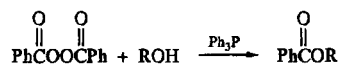
JOC 58 7286 (1996)

ROLi

CC 744 (1987)

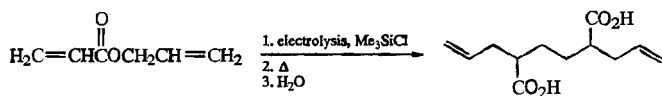
JOC 52 2113 (1987)

TL 29 1673 (1988)

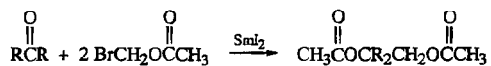


JOC 53 2300 (1988)

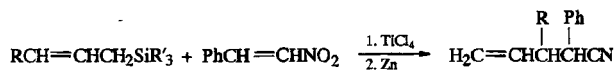
10. MISCELLANEOUS REACTIONS



TL 33 3847 (1992)



TL 32 2433 (1991)



BCSJ 59 1267 (1986)

TRANSFORMATION INDEX

The following index tabulates all organic transformations covered in this book. It describes in the first column the organic product of the transformation, in the second column the organic starting material, and in the last column the page on which that transformation occurs. Inorganic reagents, which do not introduce a carbon into the final product, and reagents that simply introduce a heteroatom, such as oxygen, sulfur and nitrogen have not been indexed. Transformations of the type $A \rightarrow B \rightarrow C$ have been indexed as follows: to C from B, to C from A, and to B from A. In equations with many variables, such as various electrophiles, nucleophiles and substituents, an attempt has been made to specify the exact transformations present in the literature, but sometimes transformations not actually in the literature have been indexed as well. The reader will have to check the original literature for specifics.

Each transformation has been indexed in its most general form. The reader is cautioned that for reactions whose scope is ill-defined, the author has often had to make assumptions as to a reaction's generality in order to index it. Not only the presence of key functional groups, but also the presence of carbon-carbon double or triple bonds and aryl groups have been considered carefully in the indexing of all transformations. The reader should keep in mind that not all reactions general for both aldehydes and ketones may have been illustrated as such in the text. It is, therefore, advisable for the reader to look under both alkanal (aldehyde) and alkanone (ketone) for a given reaction and to check the original literature.

To shorten an already lengthy index and to increase its utility, the names of key functional groups have often been simplified. For example, trialkylsilyl has been shortened to silyl, alkylthio or arylthio to thio, etc. The halogens have not been differentiated from one another. Alkyl or aryl groups that are not central to the transformation in question have been ignored.

Current IUPAC and Chemical Abstracts nomenclature has been employed in this index with the former given preference. Substitutive nomenclature has been given preference over radicofunctional, additive, subtractive, conjunctive or replacement nomenclature, except where this becomes unwieldy. With many bicyclic and polycyclic compounds bearing heteroatoms, standard bicyclic or polycyclic oxa, aza, and thia replacement nomenclature has often been used. With certain functional groups, where the names are rather complex and probably not familiar to most organic chemists, such as ylides, those compounds have simply been named as sulfur, tellurium and arsonic ylides. Metal carbenes have been treated similarly. With more complex functionality and many heterocycles, the Beilstein Commander Crossfire nomenclature system has been used with certain modifications.

Prefixes for all names are listed in alphabetical order, not in order of complexity. The following less obvious prefixes have been employed for the group or metal indicated; lithio (Li), beryllio (Be), borio (B), halo (F, Cl, Br, I), sodio (Na), magnesio (Mg), aluminio (Al), silyl (Si), thio (SR), mercapto (SH), potassio (K), calcio (Ca), titanio (Ti), vanadio (V), chromio (Cr), manganio (Mn), ferrio (Fe), cobaltio (Co), nickelio (Ni), cuprio (Cu), zincio (Zn), gallio (Ga), germyl (Ge), arsenio (As), seleno (Se), strontio (Sr), yttrio (Y), zirconio (Zr), niobio (Nb), molybdenio (Mo), rhodio (Rh), palladio (Pd), argentio (Ag), cadmio (Cd), indio (In), stannyl (Sn), antimonio (Sb), tellurio

(Te), bario (Ba), lanthanio (La), cerio (Ce), samario (Sm), ytterbio (Yb), hafnio (Hf), tantalio (Ta), mercurio (Hg), thallio (Tl), plumbyl (Pb), bismuthio (Bi), and uranio (U).

The suffix is assigned according to the principal functional group, keeping in mind the following priorities: cation > alkanolic acid > alkanoate ester > acyl halide > alkanamide > alkanenitrile > alkanal > alkanone > alkanol. With certain functional groups, where the priority may not be obvious, such as carbamates and alkanamides, such compounds have occasionally been named in more than one way. The reader is encouraged to try more than one possibility if he or she is having difficulties deciding on a name.

The principle chain in acyclic compounds has been assigned according to the following criteria applied successively: (1) maximum number of principal groups, (2) maximum number of carbon-carbon double or triple bonds considered together, (3) maximum number of double bonds, (4) highest locant for multiple bonds, (5) lowest locant for all substituents cited as prefixes and (6) lowest locant for substituents cited first as the prefix in alphabetical order. Since this last rule in particular may have occasionally been broken, the reader is encouraged to try more than one name if in doubt. Note that this does not follow IUPAC or Chemical Abstracts rules exactly, since chain length has been ignored.

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acenaphthylene	acenaphthene	190
acenaphthylene-1,2-dione	1,2-alkanediol dihalide	1426
acenaphthylene-1,2-dione	naphthalene	1426
2H-acenaphthylene-1-one	2-haloacyl halide	1426
2H-acenaphthylene-1-one	naphthalene	1426
2H-acenaphthylene-1-one	2-(naphthalen-1-yl)alkanoic acid	1428
2-acyl-3-(acylamino)alkanoate ester	alkanamide <i>N</i> -[1-(1 <i>H</i> -benzotriazol-1-yl)alkyl]	1531
2-acyl-3-(acylamino)alkanoate ester	3-oxoalkanoate ester	1531
1-acyl-2-(2-alkenyl)cyclohexanecarboxylate ester	2-acyl-7-alkenoate ester	178
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4-acyl-2-(1-alkenyl)cyclopentanecarbonitrile	2-alkenenitrile	172
4-acyl-2-(1-alkenyl)cyclopentanecarbonitrile	1-[2-(1-alkenyl)cyclopropyl]-1-alkanone	172
1-acyl-2-(2-alkenyl)cyclopentanecarboxylate ester	2-acyl-6-alkenoate ester	178
1-acyl-2-(2-alkenyl)cyclopentanecarboxylate ester	1-halo-1-alkene	178
4-acyl-2-(1-alkenyl)cyclopentanecarboxylate ester	2-alkenoate ester	172
4-acyl-2-(1-alkenyl)cyclopentanecarboxylate ester	1-[2-(1-alkenyl)cyclopropyl]-1-alkanone	172
2-acyl-1-(1-alkenyl)cyclopropanecarboxylate ester	2-alken-1-one	150, 1347
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1-acyl-2-(1-alkenyl)-2,3-dihydro-1 <i>H</i> -indole	1,3-alkadiene	451
1-acyl-2-(1-alkenyl)-2,3-dihydro-1 <i>H</i> -indole	alkanamide <i>N</i> -(2-haloaryl)	451
1-acyl-2-(1-alkenyl)-3-hydroxycyclobutanecarboxylate ester	2-acyl-4,5-epoxy-6-alkenoate ester	1059
1-acyl-2-(2-alkenyl)piperidine	1-acyl-2-sulfonylpiperidine	370
1-acyl-2-(2-alkenyl)piperidine	1-acyl-1,2,3,4-tetrahydropyridine	370
1-acyl-2-(2-alkenyl)piperidine	3-silyl-1-alkene	370
2-acyl-1-(2-alkenyl)-1,2,3,4-tetrahydroisoquinoline	acyl halide	1954
2-acyl-1-(2-alkenyl)-1,2,3,4-tetrahydroisoquinoline	3,4-dihydroisoquinoline	1954
2-acyl-1-(2-alkenyl)-1,2,3,4-tetrahydroisoquinoline	3-stannyl-1-alkene	1954
1-acyl-2-(1-alkenyl)-1,2,3,4-tetrahydropyridine	alkanamide <i>N</i> -(3-cyclohexenyl-methylene)	1851
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2-[2-acyl-3-(alkoxycarbonylmethyl)cyclopentyl]alkanoate ester	1-alkoxy-1-silyloxy-1-alkene	1582
2-[2-acyl-3-(alkoxycarbonylmethyl)cyclopentyl]alkanoate ester	8-oxo-2,6-alkadienoate ester	1582

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1-acyl-2-(2-alkynylidene)cyclopentane-carboxylate ester	2-acyl-6-alkynoate ester	449
1-acyl-2-(2-alkynylidene)cyclopentane-carboxylate ester	1-halo-1-alkyne	449
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2-acyl-2-(ω -aryl-2-alkenyl)-4-alkanohide	1, ω -alkadiene	1538
2-acyl-2-(ω -aryl-2-alkenyl)-4-alkanohide	haloarene	1538
1-acyl-2-(1-arylalkyl)cyclohexane-carboxylate ester	2-acyl-7-alkenoate ester	178
1-acyl-2-(1-arylalkyl)cyclohexane-carboxylate ester	haloarene	178
1-acyl-2-(1-arylalkyl)cyclopentane-carboxylate ester	2-acyl-6-alkenoate ester	178
1-acyl-2-(1-arylalkyl)cyclopentane-carboxylate ester	haloarene	178
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1-acyl-2-(1-haloalkyl)pyrrolidine	alkanamide <i>N</i> -(4-alkenyl)	764
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1-acyl-5-(1-hydroxyalkyl)imidazolidin-4-one	alkanal	1783
1-acyl-5-(1-hydroxyalkyl)imidazolidin-4-one	alkanone	1783
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2-acyl-3-(1-selenoalkyl)-4-alkanolide	3-oxo-2-selenoalkanoate 2-alkenyl ester	1534, 1777
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6-acyl-2-(1-sulfonylalkyl)-3-cyclohexene-carboxylate ester	2-diazoalkanoate ester	1359
1-acyl-3-(3-sulfonylalkyl)-2,3-dihydro-1 <i>H</i> -indole	alkanamide <i>N</i> -(2-alkenyl), <i>N</i> -(2-haloaryl)	170
1-acyl-3-(3-sulfonylalkyl)-2,3-dihydro-1 <i>H</i> -indole	1-sulfonyl-1-alkene	170
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2-acyl-3-alkanelactam	3-alken-3-olide	1921
2-acyl-3-alkanelactam	2-diazo-3-oxoalkanamide	1330, 1924, 1925
2-acyl-4-alkanelactam	3-amino-2-alkenamide <i>N</i> -(2-alkenyl)	1533, 1545, 1895
2-acyl-4-alkanelactam	2-diazo-3-oxoalkanamide	1330, 1924, 1925

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alkanamide	alkanamide <i>N</i> -(1-haloalkyl)	1791
alkanamide	alkanamide <i>N</i> -(1-hydroxyalkyl)	1791
alkanamide	alkanamide <i>N</i> -[1-(2-nitroaryl)alkyl]	1982
alkanamide	alkane	1626
alkanamide	alkanenitrile	1626, 1631, 1639, 1645, 1958, 1988–1990
alkanamide	alkanethioate <i>S</i> -alkyl ester	1975, 1976
alkanamide	alkanethioic acid	1949
alkanamide	alkanoate 1-(acylamino)alkyl ester	1791
alkanamide	alkanoate 1-alkenyl ester	1973, 1974
alkanamide	alkanoate ester	1973–1975
alkanamide	alkanoic acid	1264, 1714, 1941–1949, 1958, 1979
alkanamide	alkanoic acid anhydride	1957, 1958, 1979
alkanamide	alkanoic acid carbonic acid anhydride	1958
alkanamide	alkanol (1°, 2°, 3°)	1989
alkanamide	alkanone	67, 1713, 1845–1847, 1980, 1989
alkanamide	alkanone acetal	1980
alkanamide	alkanone imine	1847
alkanamide	alkanone oxime	1845, 1846
alkanamide	2-alkanamide	23, 24, 1812, 1813, 1817, 1825, 1826
alkanamide	ω -alkanamide	8
alkanamide	alkene	1631, 1701, 1778
alkanamide	2-(1-alkoxyalkoxy)-1,3-alkanedinitrile	1703
alkanamide	2-alkoxy-2-(dialkoxyposphoryl)-alkanenitrile	1713
alkanamide	alkylammonium salt	1975
alkanamide	aluminum amide	1975

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alkanamide	amine (1°, 2°)	1702, 1850, 1941- 1948, 1957
alkanamide	amine (2°)	1658, 1703, 1713, 1714, 1848, 1954, 1974- 1976, 1978, 1990
alkanamide	amine oxide	1954, 1957
alkanamide	azidoalkane	1846, 1949
alkanamide	5-azido-1-alkanone	1847
alkanamide	borioalkane	1788
alkanamide	carbamate <i>O</i> -(2-alkenyl)	1954, 1958
alkanamide	carbon monoxide	1701, 1702
alkanamide	cuprioalkane	1817, 1826
alkanamide	dialkylammonium salt	1975
alkanamide	diazoalkane	1850
alkanamide	2-diazo-1-alkanone	1850
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alkanamide	formamide	1948
alkanamide	formamide <i>N,N</i> -dialkyl	1701, 1702
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alkanamide	haloalkane	1639, 1641, 1702, 1703, 1778, 1780, 1781, 1788, 1789, 1812, 1825, 1826, 1979, 1980, 1989
alkanamide	haloformate ester	1958
alkanamide	2-halo-2-sulfonyl-1-alkanone	1848
alkanamide	isocyanate	1703, 1948
alkanamide	lithioalkane	1702, 1817, 1826
alkanamide	lithium amide	1713, 1974
alkanamide	magnesiumalkane	1702, 1703, 1792, 1817, 1826
alkanamide	magnesium amide	1975
alkanamide	mercurioalkane	1813
alkanamide	oxaziridine	1847
alkanamide	phosphoramidic dihalide <i>N,N</i> -dialkyl	1948
alkanamide	phosphoric triamide hexaalkyl	1949
alkanamide	phosphorous triamide hexaalkyl	1949
alkanamide	potassium amide	1974
alkanamide	2-(2-silylalkoxy)-1,3-benzodithiole 1,1,3,3-tetraoxide	1703
alkanamide	silylamine	1954
alkanamide	sodium amide	1974
alkanamide	3-stannylalkanamide	1788
alkanamide	stannyl amide	1975
alkanamide	sulfate dialkyl	1979, 1980
alkanamide	2-sulfonylalkanamide	60
alkanamide	2-thioalkanamide	59
alkanamide	titanium amide	1975
alkanamide	triaryl(dihalomethylene)phosphorane	1713
alkanamide	2,2,2-trihalo-1-alkanone	1668

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alkanamide	urea <i>N</i> -acyl	1948
alkanamide	zincioalkane	1792
alkanamide <i>N</i> -[2-(acylamino)alkyl]	acyl halide	839
alkanamide <i>N</i> -[2-(acylamino)alkyl]	alkanamide	77, 1789
alkanamide <i>N</i> -[2-(acylamino)alkyl]	1,2-alkanedione	839
alkanamide <i>N</i> -(2-acyl-3-oxoalkyl)	acyl halide	1526
alkanamide <i>N</i> -(2-acyl-3-oxoalkyl)	alkanal	1526
alkanamide <i>N</i> -(2-acyl-3-oxoalkyl)	1,3-alkanedione	1526
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alkanamide <i>N</i> -(alkanesulfonyl)	alkanamide <i>N</i> -(alkanesulfonyl) (alkylation)	1801
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alkanamide <i>N</i> -(alkanesulfonyl)	alkanoic acid	1990
alkanamide <i>N</i> -(alkanesulfonyl)	2-alkanamide <i>N</i> -(alkanesulfonyl)	24, 1817, 1826
alkanamide <i>N</i> -(alkanesulfonyl)	haloalkane	1801, 1826
alkanamide <i>N</i> -(alkanesulfonyl)	lithioalkane	1817
alkanamide <i>N</i> -(alkanesulfonyl)	magnesiumalkane	1817, 1826
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alkanamide <i>N</i> -(2-alkenyl)	1-acylaziridine	331
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alkanamide <i>N</i> -(2-alkenyl)	alkanenitrile	1629, 1989
alkanamide <i>N</i> -(2-alkenyl)	alkanimidate 2-alkenyl ester	1858
alkanamide <i>N</i> -(2-alkenyl)	alkanoate 2-alkenyl ester	1989
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alkanamide <i>N</i> -(2-alkenyl)	haloalkane	1790
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alkanamide <i>N</i> -(2-alkenyl)	3-seleno-1-alkene	1857
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alkanamide <i>N</i> -(4-aryl-4-oxoalkyl)	4-alkanellactam <i>N</i> -acyl	1418
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2-[2-(alkoxycarbonyl)alkylidene]-3-oxocyclopentanecarboxylate ester	3-haloalkanoate ester	1744
2-alkoxycarbonyl-4-alkylidene-2-thio-5-alkanolide	2-diazo-1,3-alkanedioate alkyl 2-(1-thioalkyl)-2-alkenyl diester	1924
1-[4-(alkoxycarbonyl)alkyl]-2-oxocycloalkanecarboxylate ester	2-oxocycloalkanecarboxylate ester	1301
1-[4-(alkoxycarbonyl)alkyl]-2-oxocycloheptanecarboxylate ester	2-oxocycloheptanecarboxylate ester	1301
1-[4-(alkoxycarbonyl)alkyl]-2-oxocyclohexanecarboxylate ester	2-oxocyclohexanecarboxylate ester	1301
3-[2-(alkoxycarbonylamino)acyl]-oxazolidin-2-one	3-acyloxazolidin-2-one	874, 1795
2-(alkoxycarbonylamino)alkanamide	2-(alkoxycarbonylamino)alkanamide (alkylation)	1782
2-(alkoxycarbonylamino)alkanamide	haloalkane	1782
3-(alkoxycarbonylamino)alkanamide	3-alkanolactam <i>N</i> -(alkoxycarbonyl)amine (1°)	1991
3-(alkoxycarbonylamino)alkanamide	2-oxoazetidine-1-carboxylate ester	1991
4-(alkoxycarbonylamino)alkanamide	4-alkanolactam <i>N</i> -(alkoxycarbonyl)amine (1°)	1991
4-(alkoxycarbonylamino)alkanamide		1991

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4-(alkoxycarbonylamino)alkanamide	2-oxopyrrolidine-1-carboxylate ester	1991
5-(alkoxycarbonylamino)alkanamide	5-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
5-(alkoxycarbonylamino)alkanamide	amine (1°)	1991
5-(alkoxycarbonylamino)alkanamide	amine (2°)	1991
5-(alkoxycarbonylamino)alkanamide	2-oxopiperidine-1-carboxylate ester	1991
6-(alkoxycarbonylamino)alkanamide	6-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
6-(alkoxycarbonylamino)alkanamide	amine (2°)	1991
6-(alkoxycarbonylamino)alkanamide	2-oxoazepane-1-carboxylate ester	1991
3-(alkoxycarbonylamino)alkanamide <i>N</i> -(alkanesulfonyl)	alkanamide <i>N</i> -(alkanesulfonyl)	1801
3-(alkoxycarbonylamino)alkanamide <i>N</i> -(alkanesulfonyl)	carbamate <i>N</i> -alkylidene	1801
2-alkoxycarbonylamino-1,4-alkanedioate diester	2-acyloxy-2-(alkoxycarbonylamino)-alkanoate ester	799
2-alkoxycarbonylamino-1,4-alkanedioate diester	2-alkoxycarbonylamino-1,4-alkanedioate diester (alkylation)	1743
2-alkoxycarbonylamino-1,4-alkanedioate diester	haloalkane	1743
2-alkoxycarbonylamino-1,4-alkanedioate diester	2-haloalkanoate ester	799
2-alkoxycarbonylamino-1,5-alkanedioate diester	2-alkoxycarbonylamino-1,5-alkanedioate diester (alkylation)	1743
2-alkoxycarbonylamino-1,5-alkanedioate diester	haloalkane	1743
2-(alkoxycarbonylamino)alkanenitrile	carbamate	800
2-(alkoxycarbonylamino)alkanenitrile	carbamate <i>N</i> -[1-(alkylperoxy)alkyl]	800
2-(alkoxycarbonylamino)alkanenitrile	silyl cyanide	800
3-(alkoxycarbonylamino)alkanenitrile	aluminum cyanide	804
3-(alkoxycarbonylamino)alkanenitrile	aziridine-1-carboxylate ester	804
3-(alkoxycarbonylamino)alkanenitrile	silyl cyanide	804
3-(alkoxycarbonylamino)alkanenitrile	sodium cyanide	804
4-(alkoxycarbonylamino)alkanenitrile	alkanenitrile	804
4-(alkoxycarbonylamino)alkanenitrile	aziridine-1-carboxylate ester	804
2-(alkoxycarbonylamino)alkanoate ester	alkanoate ester	874, 1731, 1751
2-(alkoxycarbonylamino)alkanoate ester	2-(alkoxycarbonylamino)alkanoate ester (alkylation)	1735
2-(alkoxycarbonylamino)alkanoate ester	1-alkoxy-1-silyloxy-1-alkene	1751
2-(alkoxycarbonylamino)alkanoate ester	haloalkane	1735
3-(alkoxycarbonylamino)alkanoate ester	3-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
3-(alkoxycarbonylamino)alkanoate ester	alkanoate ester	1727, 1750
3-(alkoxycarbonylamino)alkanoate ester	3-(alkoxycarbonylamino)alkanoate ester (alkylation)	1739
3-(alkoxycarbonylamino)alkanoate ester	1-alkoxy-1-silyloxy-1-alkene	1750
3-(alkoxycarbonylamino)alkanoate ester	aziridine-1,2-dicarboxylate diester	802
3-(alkoxycarbonylamino)alkanoate ester	carbamate <i>N</i> -(1-alkoxyalkyl)	800, 1727, 1750
3-(alkoxycarbonylamino)alkanoate ester	carbamate <i>N</i> -alkylidene	1727
3-(alkoxycarbonylamino)alkanoate ester	haloalkane	1739
3-(alkoxycarbonylamino)alkanoate ester	2-oxoazetidine-1-carboxylate ester	1991
3-(alkoxycarbonylamino)alkanoate ester	sodium alkanoate	1991
3-(alkoxycarbonylamino)alkanoate ester	2-zincioalkanoate ester	800
5-(alkoxycarbonylamino)alkanoate ester	5-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
5-(alkoxycarbonylamino)alkanoate ester	2-oxopiperidine-1-carboxylate ester	1991
5-(alkoxycarbonylamino)alkanoate ester	sodium alkanoate	1991
6-(alkoxycarbonylamino)alkanoate ester	6-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991

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6-(alkoxycarbonylamino)alkanoate ester	2-oxazepane-1-carboxylate ester	1991
6-(alkoxycarbonylamino)alkanoate ester	sodium alkanolate	1991
2-(alkoxycarbonylamino)alkanoic acid	2-(alkoxycarbonylamino)alkanoate 1-arylalkyl ester	1967
2-(alkoxycarbonylamino)alkanoic acid	2-(alkoxycarbonylamino)alkanoate ester	1967
2-(alkoxycarbonylamino)alkanoic acid	2-(alkoxycarbonylamino)alkanoic acid (alkylation)	1720
2-(alkoxycarbonylamino)alkanoic acid	carbamate	1790
2-(alkoxycarbonylamino)alkanoic acid	carbon dioxide	1790
2-(alkoxycarbonylamino)alkanoic acid	haloalkane	1720
6-(alkoxycarbonylamino)alkanoic acid	6-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
6-(alkoxycarbonylamino)alkanoic acid	2-oxazepane-1-carboxylate ester	1991
3-alkoxycarbonylamino-4-alkanolide	3-alkoxycarbonylamino-4-alkanolide (alkylation)	1739
3-alkoxycarbonylamino-4-alkanolide	haloalkane	1739
2-alkoxycarbonylamino-4-alkenamide	2-alkoxy-2-(alkoxycarbonylamino)-alkanamide	371
2-alkoxycarbonylamino-4-alkenamide	3-silyl-1-alkene	371
2-alkoxycarbonylamino-4-alkenoate ester	2-acyloxy-2-(alkoxycarbonylamino)-alkanoate ester	371, 799
2-alkoxycarbonylamino-4-alkenoate ester	2-alkoxy-2-(alkoxycarbonylamino)-alkanoate ester	371
2-alkoxycarbonylamino-4-alkenoate ester	2-alkoxycarbonylamino-2-haloalkanoate ester	371
2-alkoxycarbonylamino-4-alkenoate ester	3-halo-1-alkene	799
2-alkoxycarbonylamino-4-alkenoate ester	3-silyl-1-alkene	371
2-alkoxycarbonylamino-5-alkenoate ester	2-alkoxycarbonylamino-3-cuprio-alkanoate ester	242
2-alkoxycarbonylamino-5-alkenoate ester	arenesulfonate 2-alkenyl ester	242
2-alkoxycarbonylamino-5-alkenoate ester	3-halo-1-alkene	242
5-alkoxycarbonylamino-2-alkenoate ester	3-[1-(alkoxycarbonyl)aziridin-2-yl]-2-alkenoate ester	802
2-alkoxycarbonylamino-4-alkenoic acid	2-(alkoxycarbonylamino)alkanoate 2-alkenyl ester	1854
3-alkoxycarbonyl-2-amino-2-alkenoic acid	3-amino-2-alkenoate ester	355
3-alkoxycarbonyl-2-amino-2-alkenoic acid	carbon dioxide	355
5-alkoxycarbonylamino-2-alken-4-olide	2-alken-4-olide	1763
5-alkoxycarbonylamino-2-alken-4-olide	carbamate <i>N</i> -(1-hydroxyalkyl)	1763
5-alkoxycarbonylamino-2-alken-4-olide	2-(silyloxy)furan	1763
2-[1-(alkoxycarbonylamino)alkyl]-2-alkenoate ester	alkanal	1764
2-[1-(alkoxycarbonylamino)alkyl]-2-alkenoate ester	2-alkenoate ester	1764
2-[1-(alkoxycarbonylamino)alkyl]-2-alkenoate ester	carbamate	1764
2-[1-(alkoxycarbonylamino)alkyl]-3-hydroxyalkanoate ester	carbamate <i>N</i> -alkylidene	1741
2-[1-(alkoxycarbonylamino)alkyl]-3-hydroxyalkanoate ester	3-hydroxyalkanoate ester	1741
3-[2-(alkoxycarbonylamino)alkyl]-1 <i>H</i> -indole	aziridine-1-carboxylate ester	804
3-[2-(alkoxycarbonylamino)alkyl]-1 <i>H</i> -indole	1 <i>H</i> -indole	804

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2-[1-(alkoxycarbonylamino)alkyl]-3-stannyl-2-alkenoate ester	carbamate <i>N</i> -(2-alkynyl)	456
2-[1-(alkoxycarbonylamino)alkyl]-3-stannyl-2-alkenoate ester	carbon dioxide	456
2-[1-(alkoxycarbonylamino)alkyl]-3-stannyl-2-alkenoate ester	sulfate dialkyl	456
2-alkoxycarbonylamino-4-alkynoate ester	2-acyloxy-2-(alkoxycarbonylamino)-alkanoate ester	799
2-alkoxycarbonylamino-4-alkynoate ester	2-alkoxycarbonylamino-3-cuprio-alkanoate ester	603
2-alkoxycarbonylamino-4-alkynoate ester	1-halo-1-alkyne	603
2-alkoxycarbonylamino-4-alkynoate ester	3-halo-1-alkyne	799
2-alkoxycarbonylamino-3-arylalkanoate ester	2-acyloxy-2-(alkoxycarbonylamino)-alkanoate ester	799
2-alkoxycarbonylamino-3-arylalkanoate ester	2-alkoxycarbonylamino-3-zincio-alkanoate ester	1755
2-alkoxycarbonylamino-3-arylalkanoate ester	1-aryl-1-haloalkane	799
2-alkoxycarbonylamino-3-arylalkanoate ester	haloarene	1755
2-alkoxycarbonylamino-2-aryl-4-oxoalkanoate ester	2-alkoxy-2-alkoxycarbonylamino-2-arylalkanoate ester	1499
2-alkoxycarbonylamino-2-aryl-4-oxoalkanoate ester	1-silyloxy-1-alkene	1499
3-alkoxycarbonylamino-2-cyanoalkanoate ester	carbamate	800
3-alkoxycarbonylamino-2-cyanoalkanoate ester	carbamate <i>N</i> -[1-(alkylperoxy)alkyl]	800
3-alkoxycarbonylamino-2-cyanoalkanoate ester	2-cyanoalkanoate ester	800
2-alkoxycarbonylamino-2-deuteroalkanoic acid	2-(alkoxycarbonylamino)alkanoic acid	1720
2-alkoxycarbonylamino-3-hydroxyalkanoate ester	alkanal	1735
2-alkoxycarbonylamino-3-hydroxyalkanoate ester	alkanone	1735
2-alkoxycarbonylamino-3-hydroxyalkanoate ester	2-(alkoxycarbonylamino)alkanoate ester	1735
5-alkoxycarbonylamino-3-hydroxyalkanoate ester	5-alkoxycarbonylamino-3-oxoalkanoate ester	1081, 1083
2-alkoxycarbonylamino-3-hydroxyalkanoic acid	alkanal	1720
2-alkoxycarbonylamino-3-hydroxyalkanoic acid	2-(alkoxycarbonylamino)alkanoic acid	1720
2-alkoxycarbonylamino-3-(1-hydroxyalkyl)-1,4-alkanedioate diester	alkanal	1743
2-alkoxycarbonylamino-3-(1-hydroxyalkyl)-1,4-alkanedioate diester	2-alkoxycarbonylamino-1,4-alkanedioate diester	1743
2-alkoxycarbonylamino-4-(1-hydroxyalkyl)-1,4-alkanedioate diester	alkanal	1743
2-alkoxycarbonylamino-4-(1-hydroxyalkyl)-1,4-alkanedioate diester	2-alkoxycarbonylamino-1,4-alkanedioate diester	1743
3-alkoxycarbonylamino-2-(1-hydroxyalkyl)alkanoate ester	alkanal	1739

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3-alkoxycarbonylamino-2-(1-hydroxy-alkyl)alkanoate ester	3-(alkoxycarbonylamino)alkanoate ester	1739
3-alkoxycarbonylamino-2-(1-hydroxy-alkyl)-5-alkanolide	alkanone	1739
3-alkoxycarbonylamino-2-(1-hydroxy-alkyl)-5-alkanolide	3-alkoxycarbonylamino-5-alkanolide	1739
2-alkoxycarbonyl-4-aminomethylene-amino-3-aryl-1,5-alkanedioate diester	2-(aminomethyleneamino)alkanoate ester	1735
2-alkoxycarbonyl-4-aminomethylene-amino-3-aryl-1,5-alkanedioate diester	2-arylmethylene-1,3-alkanedioate diester	1735
2-alkoxycarbonylamino-5-oxo-1,7-alkanedioate diester	alkanoate ester	1730
2-alkoxycarbonylamino-5-oxo-1,7-alkanedioate diester	5-oxopyrrolidine-1,2-dicarboxylate diester	1730
7-alkoxycarbonylamino-3-oxoalkanenitrile	5-alkanelactam <i>N</i> -(alkoxycarbonyl)	1803
7-alkoxycarbonylamino-3-oxoalkanenitrile	alkanenitrile	1803
7-alkoxycarbonylamino-3-oxoalkanenitrile	2-oxopiperidine-1-carboxylate ester	1803
2-alkoxycarbonylamino-4-oxoalkanoate ester	acyl halide	1395, 1397
2-alkoxycarbonylamino-4-oxoalkanoate ester	2-alkoxycarbonylamino-3-cuprio-alkanoate ester	1395
2-alkoxycarbonylamino-4-oxoalkanoate ester	2-alkoxycarbonylamino-3-zincio-alkanoate ester	1397
2-alkoxycarbonylamino-5-oxoalkanoate ester	acyl halide	1394
2-alkoxycarbonylamino-5-oxoalkanoate ester	2-alkoxycarbonylamino-4-cuprio-alkanoate ester	1394
5-alkoxycarbonylamino-3-oxoalkanoate ester	3-alkanelactam <i>N</i> -(alkoxycarbonyl)	1730
5-alkoxycarbonylamino-3-oxoalkanoate ester	alkanoate ester	1730
5-alkoxycarbonylamino-3-oxoalkanoate ester	2-oxoazetidine-1-carboxylate ester	1730
7-alkoxycarbonylamino-3-oxoalkanoate ester	5-alkanelactam <i>N</i> -(alkoxycarbonyl)	1730
7-alkoxycarbonylamino-3-oxoalkanoate ester	alkanoate ester	1730
7-alkoxycarbonylamino-3-oxoalkanoate ester	2-oxopiperidine-1-carboxylate ester	1730
3-alkoxycarbonylamino-2-(silyloxy)-alkanamide	carbamate <i>N</i> -(1-alkoxyalkyl)	1782
3-alkoxycarbonylamino-2-(silyloxy)-alkanamide	2-(silyloxy)alkanamide	1782
2-(alkoxycarbonyl)arenecarboxylic acid	arenecarboxylate ester	1682
2-(alkoxycarbonyl)arenecarboxylic acid	carbon dioxide	1682
2-[2-(alkoxycarbonyl)aryl]alkanoic acid	arenecarboxylate ester	89
2-[2-(alkoxycarbonyl)aryl]alkanoic acid	carbon dioxide	89
3-alkoxycarbonyl-3-aza-1,5-alkanedioate diester	3-alkoxycarbonyl-3-aza-1,5-alkanedioate diester (alkylation)	1744
3-alkoxycarbonyl-3-aza-1,5-alkanedioate diester	haloalkane	1744

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2-alkoxycarbonyl-3,4-benzo-4-alkanelactam	2-(<i>N</i> -arylcarbamoyl)-2-diazoalkanoate ester	1924
4-alkoxycarbonyl-2,3-benzo-5-alkanelactam	alkanal imine	1907
4-alkoxycarbonyl-2,3-benzo-5-alkanelactam	isochroman-1,3-dione	1907
2-alkoxycarbonyl-4-cyano-1,5-alkanedioate diester	2-alkylidene-1,3-alkanedioate diester	1836
2-alkoxycarbonyl-4-cyano-1,5-alkanedioate diester	2-cyanoalkanoate ester	1836
(6-alkoxycarbonyl-3-cyclohexenyl)-trialkylammonium salt	1,3-alkadiene	540
(6-alkoxycarbonyl-3-cyclohexenyl)-trialkylammonium salt	(2-alkoxycarbonyl-1-alkenyl)-trialkylammonium salt	540
2-(alkoxycarbonyl)cyclopropane-carboxylic acid	2-alkenoate ester	146, 1719
2-(alkoxycarbonyl)cyclopropane-carboxylic acid	2-haloalkanoic acid	1719
2-(alkoxycarbonyl)cyclopropane-carboxylic acid	sulfur ylide	146
3-[1-(alkoxycarbonyl)cyclopropyl]-2-alkenoate ester	2-alkene-1,5-dioate diester	158
3-[1-(alkoxycarbonyl)cyclopropyl]-2-alkenoate ester	1,3,2-dioxathiolane 2,2-dioxide	158
3-[1-(alkoxycarbonyl)cyclopropyl]-2-alkenoate ester	sulfate cyclic	158
2-[2-(alkoxycarbonyl)cyclopropyl]-1-alkenylphosphonamide	2-alkenoate ester	140
2-[2-(alkoxycarbonyl)cyclopropyl]-1-alkenylphosphonamide	3-halo-2-alkenylphosphonamide	140
2-alkoxycarbonyl-3,3-diaryl-2-alkenoic acid	carbon dioxide	354
2-alkoxycarbonyl-3,3-diaryl-2-alkenoic acid	3,3-diaryl-2-alkenoate ester	354
2-[3-(alkoxycarbonyl)-2,2-dihalocyclopropyl]alkanoate ester	alkanoate ester	159
2-[3-(alkoxycarbonyl)-2,2-dihalocyclopropyl]alkanoate ester	4,4,4-trihalo-2-alkenoate ester	159
2-alkoxycarbonyl-1,2-dihydro-naphthalene-2-carboxylic acid	haloformate ester	1824
2-alkoxycarbonyl-1,2-dihydro-naphthalene-2-carboxylic acid	lithioalkane	1824
2-alkoxycarbonyl-1,2-dihydro-naphthalene-2-carboxylic acid	2-(naphthalen-2-yl)-4,5-dihydrooxazole	1824
2-alkoxycarbonyl-2,3-epoxyalkanoic acid	carbon dioxide	886
2-alkoxycarbonyl-2,3-epoxyalkanoic acid	2,3-epoxyalkanoate ester	886
2-alkoxycarbonylhalomethyl-3-silylpyrrolidine-1-carboxylate ester	alkanal acetal	866
2-alkoxycarbonylhalomethyl-3-silylpyrrolidine-1-carboxylate ester	carbamate	866
2-alkoxycarbonylhalomethyl-3-silylpyrrolidine-1-carboxylate ester	2-halo-3-silyl-4-alkenoate ester	866
3-alkoxycarbonyl-2-hydroxy-4-alkanelactam <i>N</i> -aryl	alkanal aryl imine	1922

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3-alkoxycarbonyl-2-hydroxy-4-alkane-lactam <i>N</i> -aryl	2-hydroxy-1,4-alkanedioate diester	1922
5-alkoxycarbonyl-4-hydroxy-2-alkenoic acid	3-acylthiazolidine-2-thione	1798
5-alkoxycarbonyl-4-hydroxy-2-alkenoic acid	alkanol (1°, 2°, 3°)	1798
5-alkoxycarbonyl-4-hydroxy-2-alkenoic acid	4-hydroxy-2-alken-4-olide	1798
5-alkoxycarbonyl-4-hydroxy-2-alkenoic acid	4-hydroxy-6-oxo-6-(2-thioxothiazolidin-3-yl)-2-alkenoic acid	1798
[3-alkoxycarbonyl-2-(hydroxy)alkyl]-triarylphosphonium salt	2,3-epoxyalkanoate ester	1043
[3-alkoxycarbonyl-2-(hydroxy)alkyl]-triarylphosphonium salt	triarylphosphine	1043
2-alkoxycarbonylmethyl-6-aminocyclohexanecarboxylate ester	2,7-alkadiene-1,9-dioate diester	770
8-alkoxycarbonylmethyl-1-azabicyclo-[5.3.0]dec-9-ene-8,9-dicarboxylate diester	2-alkyne-1,4-dioate diester	862
8-alkoxycarbonylmethyl-1-azabicyclo-[5.3.0]dec-9-ene-8,9-dicarboxylate diester	3-(azepan-1-yl)-2-alkenoate ester	862
7-alkoxycarbonylmethyl-1-azabicyclo-[4.3.0]non-8-ene-7,8-dicarboxylate diester	2-alkyne-1,4-dioate diester	862
7-alkoxycarbonylmethyl-1-azabicyclo-[4.3.0]non-8-ene-7,8-dicarboxylate diester	3-(piperidin-1-yl)-2-alkenoate ester	862
4-alkoxycarbonylmethyl-1-azabicyclo-[3.3.0]oct-2-ene-3,4-dicarboxylate diester	2-alkyne-1,4-dioate diester	862
4-alkoxycarbonylmethyl-1-azabicyclo-[3.3.0]oct-2-ene-3,4-dicarboxylate diester	3-(pyrrolidin-1-yl)-2-alkenoate ester	862
9-alkoxycarbonylmethyl-1-azabicyclo-[6.3.0]undec-10-ene-9,10-dicarboxylate diester	2-alkyne-1,4-dioate diester	862
9-alkoxycarbonylmethyl-1-azabicyclo-[6.3.0]undec-10-ene-9,10-dicarboxylate diester	3-(azocan-1-yl)-2-alkenoate ester	862
3-alkoxycarbonylmethyl-2,3-dihydro-1 <i>H</i> -pyrrole-3,4-dicarboxylate diester	2-alkyne-1,4-dioate diester	862
3-alkoxycarbonylmethyl-2,3-dihydro-1 <i>H</i> -pyrrole-3,4-dicarboxylate diester	3-amino-2-alkenoate ester	862
2-[1-(4-alkoxycarbonylmorpholin-2-on-3-yl)alkyl]-1,3-alkanedioate diester	2-alkylidene-1,3-alkanedioate diester	1737
2-[1-(4-alkoxycarbonylmorpholin-2-on-3-yl)alkyl]-1,3-alkanedioate diester	morpholin-2-one-4-carboxylate ester	1737
2-alkoxycarbonyl-3-oxoalkanoic acid	acyl halide	1720
2-alkoxycarbonyl-3-oxoalkanoic acid	2-(alkoxycarbonyl)alkanoic acid	1720
4-alkoxycarbonyl-3-oxoalkanoic acid	carbon dioxide	1541
4-alkoxycarbonyl-3-oxoalkanoic acid	3-oxoalkanoate ester	1541
5-alkoxycarbonyl-4-oxoalkanoic acid	1,4-alkanedioic acid anhydride	1401
5-alkoxycarbonyl-4-oxoalkanoic acid	2-haloalkanoate ester	1401

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5-alkoxycarbonyl-5-oxoalkanoic acid	2-oxocyclopentanecarboxylate ester	1669
6-alkoxycarbonyl-5-oxoalkanoic acid	1,5-alkanedioic acid anhydride	1401
6-alkoxycarbonyl-5-oxoalkanoic acid	2-haloalkanoate ester	1401
6-alkoxycarbonyl-6-oxoalkanoic acid	2-oxocyclohexanecarboxylate ester	1669
1-[4-(alkoxycarbonyl)-2-oxoalkyl]-cyclopentanecarboxylate ester	2-oxocyclopentanecarboxylate ester	1301
2-(4-alkoxycarbonyl-2-oxomorpholin-3-yl)-1,3-alkanedioate diester	1,3-alkanedioate diester	1774
2-(4-alkoxycarbonyl-2-oxomorpholin-3-yl)-1,3-alkanedioate diester	3-halo-2-oxomorpholine-4-carboxylate ester	1774
2-(4-alkoxycarbonyl-2-oxomorpholin-3-yl)alkanoate ester	alkanoate ester	1750
2-(4-alkoxycarbonyl-2-oxomorpholin-3-yl)alkanoate ester	1-alkoxy-1-silyloxy-1-alkene	1750, 1774
2-(4-alkoxycarbonyl-2-oxomorpholin-3-yl)alkanoate ester	3-halo-2-oxomorpholine-4-carboxylate ester	1750, 1774
3-[2-(alkoxycarbonyloxy)acyl]-oxazolidin-2-one	3-acyloxazolidin-2-one	1795
3-[2-(alkoxycarbonyloxy)acyl]-oxazolidin-2-one	peroxide di(alkoxycarbonyl)	1795
1-(alkoxycarbonyl)pyrrolidine-2-carboxylic acid	carbon dioxide	1790
1-(alkoxycarbonyl)pyrrolidine-2-carboxylic acid	pyrrolidine-1-carboxylate ester	1790
4-[1-(alkoxycarbonyl)pyrrolidin-2-yl]-2-alken-4-olide	2-alken-4-olide	1763
4-[1-(alkoxycarbonyl)pyrrolidin-2-yl]-2-alken-4-olide	2-alkoxypyrrolidine-1-carboxylate ester	1763
4-[1-(alkoxycarbonyl)pyrrolidin-2-yl]-2-alken-4-olide	2-(alkylperoxy)pyrrolidine-1-carboxylate ester	1763
4-[1-(alkoxycarbonyl)pyrrolidin-2-yl]-2-alken-4-olide	2-(silyloxy)furan	1763
2-alkoxycarbonyl-3-(1-selenoalkyl)-4-alkanelactam <i>N</i> -(2-alkenyl)	2-[<i>N,N</i> -di(2-alkenyl)carbamoyl]-2-selenoalkanoate ester	1777, 1786
2-alkoxycarbonyl-3-(1-selenoalkyl)-4-alkanolide	2-seleno-1,3-alkanedioate 2-alkenyl alkyl diester	1777
2-alkoxy-2-cyanoalkanoate ester	2-alkoxyalkanoate ester	1733
2-alkoxy-2-cyanoalkanoate ester	cyanogen	1733
4-alkoxy-2-cyano-5-alkenoate ester	1-alkoxy-3-titanio-1-alkene	1823
4-alkoxy-2-cyano-5-alkenoate ester	2-cyano-2-alkenoate ester	1823
(alkoxycyanomethylene)cyclopropaarene	disilylcyclopropaarene	340
(alkoxycyanomethylene)cyclopropaarene	haloformate ester	340
2-alkoxycycloalkanone	1-alkoxy-1-lithio-1-sulfonylalkane	1293
2-alkoxycycloalkanone	1-(1-alkoxy-1-sulfonylalkyl)cycloalkanol	1293
2-alkoxycycloalkanone	cycloalkanone	1293
2-alkoxy-3-cycloalkenol	ω -alkoxy- ω -stannyl- ω -alkenal	1167
3-alkoxycyclobutane-1,1,2,2-tetracarbonitrile	1-alkoxy-1-alkene	162
3-alkoxycyclobutane-1,1,2,2-tetracarbonitrile	tetracyanoethylene	162
2-alkoxycyclobutanone	alkene	1343
2-alkoxycyclobutanone	4-alken-1-ol	1343
2-alkoxycyclobutanone	chromium carbene	1343
3-alkoxycyclodecanone	9-silyloxy-9-alkenal acetal	1501
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arenesulfonamide <i>N</i> -(arenesulfonyl)	amine (1°)	270
arenesulfonamide <i>N</i> -(2-aryl-3-alkenyl)	2-(1-alkenyl)-1-(arenesulfonyl)aziridine	806
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arenesulfonamide <i>N</i> -(2-hydroxy-3-stannylalkyl)	1-arenesulfonyl-2-(1-hydroxyalkyl)-aziridine	807
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arenesulfonamide <i>N</i> -(2-oxoalkyl)	1-silyloxy-1-alkene	865
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3,4-benzo-4-alkanelactam	2-diazoalkanamide <i>N</i> -aryl	1924
3,4-benzo-4-alkanelactam	dithiocarbonate <i>O</i> -alkyl, <i>S</i> -[1-(<i>N</i> -arylcarbamoyl)alkyl] diester	1908
3,4-benzo-4-alkanelactam	2-haloalkanamide <i>N</i> -aryl	1907
3,4-benzo-4-alkanelactam	1 <i>H</i> -indole	1641
3,4-benzo-5-alkanelactam	alkanal	1907
3,4-benzo-5-alkanelactam	alkanamide <i>N</i> -[1-(2-haloaryl)alkyl]	1779, 1926
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3,4-benzo-5-alkanelactam	2-diazoalkanamide <i>N</i> -(1-arylalkyl)	1924
3,4-benzo-6-alkanelactam	3-azaspiro[5.5]undeca-7,10-diene-2,9-dione	1924
3,4-benzo-6-alkanelactam	2-diazoalkanamide <i>N</i> -(2-(4-alkoxyaryl)-alkyl)	1924
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5,6-benzo-6-alkanelactam	4-arylalkanamide <i>N</i> -halo	1905
3,4-benzo-4-alkanelactam <i>N</i> -acyl	1-acyl-1 <i>H</i> -indole	1675
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2,3-benzo-4-alkanolide	alkanone	1903, 1906
2,3-benzo-4-alkanolide	arenecarboxamide	1906
2,3-benzo-4-alkanolide	arenecarboxylate ester	1906
2,3-benzo-4-alkanolide	arenecarboxylic acid	1862
2,3-benzo-4-alkanolide	arene-1,2-dicarboxylic acid anhydride	1677, 1678
2,3-benzo-4-alkanolide	1-aryl-1-alkanol	1905
2,3-benzo-4-alkanolide	carbamate <i>O</i> -[1-(2-haloaryl)alkyl]	1902
2,3-benzo-4-alkanolide	carbon dioxide	1905
2,3-benzo-4-alkanolide	carbon monoxide	1695, 1902, 1905
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2,3-benzo-4-alkanolide	2-haloarenecarboxylate ester	1903
2,3-benzo-4-alkanolide	2-haloarenecarboxylic acid	1903
2,3-benzo-4-alkanolide	1-(2-haloaryl)-1-alkanol	1695, 1902
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2,3-benzo-4-alkanolide	isobenzofuran-1,3-dione	1677, 1678
2,3-benzo-4-alkanolide	triflate 2-(1-hydroxyalkyl)aryl ester	1902
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carbamate <i>N</i> -(5-aryl-5-oxoalkyl)	magnesiorene	1419
carbamate <i>N</i> -(5-aryl-5-oxoalkyl)	2-oxopiperidine-1-carboxylate ester	1419
carbamate <i>N</i> -(6-aryl-6-oxoalkyl)	6-alkanelactam <i>N</i> -(alkoxycarbonyl)	1419
carbamate <i>N</i> -(6-aryl-6-oxoalkyl)	magnesiorene	1419
carbamate <i>N</i> -(6-aryl-6-oxoalkyl)	2-oxopiperidine-1-carboxylate ester	1419
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carbamate <i>N</i> -(3-carbamoylalkyl)	4-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
carbamate <i>N</i> -(3-carbamoylalkyl)	amine (1°)	1991
carbamate <i>N</i> -(3-carbamoylalkyl)	2-oxopyrrolidine-1-carboxylate ester	1991
carbamate <i>N</i> -(4-carbamoylalkyl)	5-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
carbamate <i>N</i> -(4-carbamoylalkyl)	amine (1°)	1991
carbamate <i>N</i> -(4-carbamoylalkyl)	amine (2°)	1991
carbamate <i>N</i> -(4-carbamoylalkyl)	2-oxopiperidine-1-carboxylate ester	1991
carbamate <i>N</i> -(5-carbamoylalkyl)	6-alkanelactam <i>N</i> -(alkoxycarbonyl)	1991
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3-oxo-4-cyclopentene-1,2-dicarboxylate diester	2-alkynoate aryl ester	1743
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5-oxo-2,5-dihydro-1 <i>H</i> -pyrrole-3- carboxylate ester	carbon monoxide	1900
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2-(2-oxooxazolidin-3-yl)-3-alkanelactam	2-(2-oxooxazolidin-3-yl)-3-alkanelactam (alkylation)	1782
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2-oxo-3-(3-oxoalkyl)-4-alkenoate ester	2,4-dioxoalkanoate ester	553
2-oxo-1-(4-oxoalkyl)cycloalkane- carboxylate ester	2-oxocycloalkanecarboxylate ester	1301
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3-{4-oxo-4-(2-oxooxazolidin-3-yl)- acyl}oxazolidin-2-one	3-acyloxazolidin-2-one	1795
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2-[3-oxo-3-(2-oxooxazolidin-3-yl)alkyl]-2-alkenoate ester	2-[1-(acyloxy)alkyl]-2-alkenoate ester	1793
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3-(2-oxopiperidin-1-yl)alkanoate ester	5-alkanelactam	1981
3-(2-oxopiperidin-1-yl)alkanoate ester	2-alkenoate ester	1981
2-oxo-5-(pyridin-2-ylthiocarbonyl)alkanoate ester	alkanethioate S-(pyridin-2-yl) ester	1754
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3-(2-oxopyrrolidin-1-yl)-2-alkenoate ester	2-alkenoate ester	1981
3-(2-oxopyrrolidin-1-yl)-2-alken-1-one	4-alkanelactam	1981
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2,3,4,7-tetrahydro-1 <i>H</i> -azepine	5-amino-1-silyl-1-alkene	865
2,3,4,5-tetrahydro-1 <i>H</i> -benzo[<i>b</i>]azepine	2-(5-silyl-3-alkenyl)-1-tetralone <i>O</i> -(alkanesulfonyl) oxime	862
1,3,4,5-tetrahydrobenzo[<i>b</i>]azepin-2-one	4-alkenamide <i>N</i> -(2-haloaryl)	181
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2,3,4,5-tetrahydrobenzo[<i>c</i>]azepin-1-one	1-amino-3-(2-haloaryl)alkane	1702, 1902
2,3,4,5-tetrahydrobenzo[<i>c</i>]azepin-1-one	carbon monoxide	1702, 1902
2,3,4,5-tetrahydrobenzo[<i>c</i>]azepin-1-one	triflate 2-(3-aminoalkyl)aryl ester	1902
6,7,8,9-tetrahydro-5 <i>H</i> -benzocycloheptene	5-aryl-1-alkanol	132
6,7,8,9-tetrahydro-5 <i>H</i> -benzocycloheptene-5-carbonitrile	6-arylalkanenitrile chromium tricarbonyl	1803
6,7,8,9-tetrahydro-5 <i>H</i> -benzocycloheptene-5-carbonitrile	6-(2-haloaryl)alkanenitrile	177
6,7,8,9-tetrahydrobenzocycloheptene-5,5-dicarboxylate diester	2-(4-arylalkyl)-1,3-alkanedioate diester	1769
2,3,4,9a-tetrahydrobenzocyclohepten-1-one	5-aryl-1-diazo-2-alkanone	1332
6,7,8,9-tetrahydrobenzocyclohepten-5-one	5-aryllacyl halide	1430
6,7,8,9-tetrahydrobenzocyclohepten-5-one	5-arylalkanoic acid	1428
6,7,8,9-tetrahydrobenzocyclohepten-5-one	cyclopentanone	1300
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7,8,9,10-tetrahydro-6H-benzocycloocten-5-one	6-arylacyl halide	1430
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3a,4,7,7a-tetrahydrobenzo-1,3-dioxole-2-thione	1,3-dioxole-2-thione	543
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4,5,6,7-tetrahydrobenzofuran	2,3-di(alkylidene)-2,3-dihydrofuran	537
4,5,6,7-tetrahydrobenzooxazole	alkene	537
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4-(tetrahydrofuran-2-yl)-2-alken-4-olide	2-alken-4-olide	1763
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4-(tetrahydrofuran-2-yl)-2-alken-1-one	4-alken-1-ol	910
4-(tetrahydrofuran-2-yl)-2-alken-1-one	2-alken-1-one	910
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tetrahydrofuro[2,3-b]pyrrol-2-one	2,3-dihydro-1 <i>H</i> -pyrrole	1877
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2,3,4,5-tetrahydro-1 <i>H</i> -indene	1-alken-6-yne	505
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1,2,3,4-tetrahydroisoquinoline	1-(1-haloalkyl)-2-(1-silylalkyl)arene	856
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